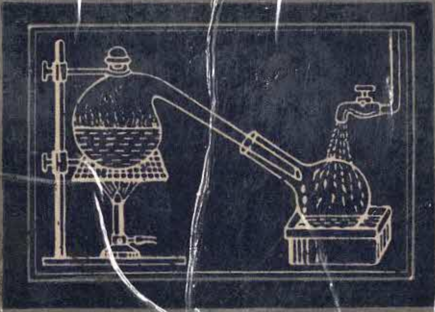
A TEXT-BOOK OF
HIGHER SECONDARY
CHEMISTRY



Dr. Satyabrata Saha

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A TEXT-BOOK OF
HIGHER SECONDARY CHEMISTRY

Written strictly in accordance with the higher secondary syllabus in chemistry prescribed by West Bengal Council for Higher Secondary Education.

A TEXT-BOOK OF HIGHER SECONDARY CHEMISTRY

● VOLUME I ●

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25/3, B.C. Road
Calcutta

BHARATI BOOK STALL
PUBLISHERS & BOOK-SELLERS
6, Ramanath Mazumdar Street
Calcutta-700 009

Published by :
Sri Ashoke Kumar Barik
Bharati Book Stall
6, Ramanath Mazumdar Street
Calcutta-700 009

540
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Date 10-8-98
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First Edition : July, 1986

Price : Rupees Fifty Only.

Printed by :
Sri Tulshi Charan Boxi
National Printing Works
33D, Madan Mitra Lane
Calcutta-700 006

PREFACE

The wide appreciation of my "A Text-Book of Higher Secondary Chemistry" given by the teachers and the students alike has encouraged me to bring out this edition. Although the book has been revised and enlarged strictly in accordance with the syllabus prescribed by West Bengal Council for Higher Secondary Education, the subject-matter has been so thoroughly and lucidly represented that it will also be helpful to the higher secondary students of other Indian Boards and Universities. The book consists of two volumes. The present volume (volume I) covers paper I of the syllabus.

Chemistry is still primarily an experimental science and students should be taught how the experimental data are interpreted properly. Yet it is the theory which provides the connective link for the experimental facts. In this book, every effort has been made to show how the experimental data are related to theory. Instead of purely descriptive approach, the analytical approach which consists mainly of describing experimental facts and describing how these are properly interpreted, is emphasised. It will greatly aid the students to extrapolate and generalise rather than just memorise.

The subject-matter of the book has been presented systematically and lucidly using simple and clear language. Details of preparative and manufacturing processes have been incorporated in various chapters devoted to descriptive chemistry. The diagrams have been drawn in a lucid style so that students may easily understand how the various phenomena are experimented. A wealth of problems have been provided so that no separate book on problems should be necessary. A large number of problems have been worked out with a view to clarify the applications of the principles. The solving of the problems by students is of great importance because there is no better test of the learning of the principles than that afforded by the necessity of applying them. The answer to each problem has been given.

At the end of each chapter, there is a number of questions of all types. This would ensure a thorough revision of the subject-matter learnt in each chapter.

It is my sincere belief that the book will be very useful to the students. I shall highly appreciate suggestions and criticisms which might improve the book. I shall be grateful if my attention is drawn to any errors which may have escaped my notice.

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Satyabrata Saha

SYLLABUS IN CHEMISTRY

Full Marks—200

PAPER—I (Marks—70)

GROUP—A

General and Physical Chemistry (Marks—40)

I. Laws of Chemical Combination—Dalton's Atomic Theory (critical study), Gay Lussac's Law. Atomic Weight.

II. Concept of the molecule and Avogadro's hypothesis. Definition of molecular weight. Simple deductions from Avogadro's hypothesis. Elementary idea about Avogadro's Number. Mole concept—numerical problems on the concept.

III. Chemical Equations—different types and their significance. Stoichiometry—weight to weight, weight to volume and volume to volume calculations. Eudiometry and problems on Eudiometry. Vapour density, empirical formulae and molecular formulae.

IV. Equivalent weights. Determination of equivalent, atomic and molecular weights (Mol. wt. by Victor Mayer's method only). Dulong and Petit's law. Mitscherlich's law of isomorphism—numerical problems.

V. Acids, bases and salts. Arrhenius concept of acids and bases. Different types of oxides, oxyacids, hydroxides and hydracids. Hydrolysis of salts. Equivalent weight of acids, bases and salts. Standard solutions : normal (and formal) and molar solutions. Neutralisation, acid-base indicator. Chemical calculations on acidimetry and alkalimetry.

VI. Boyle's law, Charles' law, Gas Constant R ; $PV=nRT$. Dalton's law of partial pressure, Graham's law of diffusion of gases. Numerical problems.

VII. Solution of solid in liquid. Solubility. Saturated, unsaturated and supersaturated solutions.
Solubility curves and determination of solubility.

Crystallisation, fractional crystallisation, water of crystallisation and its determination. Colloids and dialysis.

VIII. Conducting and non-conducting solutions—Arrhenius theory. Electrolysis—Faraday's laws of Electrolysis.

Electrochemical equivalent. $\frac{F}{N}=e$

IX. Law of Mass Action. Dynamic equilibrium and equilibrium constant. Le Chatelier's principle and its application with special reference to ammonia, nitric acid, sulphuric acid. (Note : Numerical problems on Law of Mass Action are not required).

GROUP—B

Inorganic Chemistry (Marks—30)

The chemistry of an element or a compound mentioned in this syllabus includes preparation, properties, reactions and uses.

I. Oxygen and hydrogen, water, hard and soft water : Softening of water : boiling, lime-soda process and ion-exchange method. Hydrogen peroxide and ozone.

II. Air, Nitrogen, NH_3, N_2O, NO, N_2O_4, HNO_2, HNO_3.

III. Boron (from B_2O_3 by Mg reduction), Orthoboric acid, Borax.

IV. Carbon, CO, CO_2, Carbonic acid.

V. Phosphorus, PH_3, P_4O_6, P_4O_{10}, H_3PO_3, H_3PO_4.

VI. Sulphur, H_2S, SO_2, SO_3, H_2SO_3, H_2SO_4.

VII. Halogens : Fluorine, Chlorine, Bromine and Iodine—a comparative study, Hydracids.

VIII. Large scale preparation (omitting details) with reference to the physico-chemical principles involved, wherever applicable, of the following :

Hydrogen, Ammonia, Nitric Acid, Sulphuric acid (contact process only). Coal-gas.

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SOME PHYSICAL CONSTANTS

Avogadro number	N	$6{\cdot}023 \times 10^{23}$ mole^{-1}
Charge of an electron	e	$4{\cdot}8029 \times 10^{-10}$ esu
Molar gas constant	R	$8{\cdot}315 \times 10^{7}$ erg per mole per deg.
1 Faraday	F	96,500 coulombs/mole
Velocity of light	C	3×10^{10} cm per second

SOME USEFUL INFORMATIONS

1 erg $= 1 \times 10^{-7}$ Joule $= 2{\cdot}3901 \times 10^{-8}$ calorie

1 calorie $= 4{\cdot}1840$ Joule

1 coulomb $= 3 \times 10^{9}$ esu

Normal temperature $= 0°$C or 273°A

Normal pressure $= 76$ cm of Hg

Volume of 1 mole of gas at N. T. P. $= 22{\cdot}4$ litres

weight of 1 c.c. of hydrogen at N. T. P. $= 0{\cdot}000089$ gram.

Atomic Weights

Name	Sym-bol	Atomic Number	Atomic Weight	Name	Sym-bol	Atomic Number	Atomic Weight
Actinium	Ac	89	227	Neodymium	Nd	60	144·27
Aluminium	Al	13	26·98	Neon	Ne	10	20·183
Americium	Am	95	243	Neptunium	Np	93	(237)
Antimony	Sb	51	121·76	Nickel	Ni	28	58·71
Argon	Ar	18	39·944	Niobium	Nb	41	92·91
Arsenic	As	33	74·91	Nitrogen	N	7	14·008
Astatine	At	85	210	Osmium	Os	76	190·2
Barium	Ba	56	137·36	Oxygen	O	8	16·000
Beryllium	Be	4	9·013	Palladium	Pd	46	106·40
Bismuth	Bi	83	209·00	Phosphorus	P	15	30·975
Boron	B	5	10·82	Platinum	Pt	78	195·09
Bromine	Br	35	79·916	Plutonium	Pu	94	(242)
Cadmium	Cd	48	112·41	Polonium	Po	84	(210)
Calcium	Ca	20	40·08	Potassium	K	19	39·096
Carbon	C	6	12·01	Praseodymium	Pr	59	140·92
Cerium	Ce	58	140·13	Promethium	Pm	61	145
Cesium	Cs	55	132·91	Protactinium	Pa	91	231
Chlorine	Cl	17	35·457	Radium	Ra	88	226·05
Chromium	Cr	24	52·01	Radon	Rn	86	222
Cobalt	Co	27	58·94	Rhenium	Re	75	186·22
Copper	Cu	29	63·54	Rhodium	Rh	45	102·91
Curium	Cm	96	(245)	Rubidium	Rb	37	85·48
Dysprosium	Dy	66	162·51	Ruthenium	Ru	44	101·1
Erbium	Er	68	167·27	Samarium	Sm	62	150·35
Europium	Eu	68	152·0	Scandium	Sc	21	44·96
Fluorine	F	9	19·00	Selenium	Se	34	78·96
Francium	Fr	87	(223)	Silicon	Si	14	28·09
Gadolinium	Gd	64	157·26	Silver	Ag	47	107·880
Gallium	Ga	31	69·72	Sodium	Na	11	22·991
Germanium	Ge	32	72·60	Strontium	Sr	38	87·63
Gold	Au	79	197·0	Sulphur	S	16	32·066
Hafnium	Hf	72	178·50	Tantalum	Ta	73	180·95
Helium	He	2	4·033	Technetium	Tc	43	99
Holmium	Ho	67	164·94	Tellurium	Te	52	127·61
Hydrogen	H	1	1·008	Terbium	Tb	65	158·98
Indium	In	49	114·82	Thallium	Tl	81	204·39
Iodine	I	53	126·91	Thorium	Th	90	232·05
Iridium	Ir	77	192·2	Thulium	Tm	69	168·94
Iron	Fe	26	55·85	Tin	Sn	50	118·70
Krypton	Kr	36	83·80	Titanium	Ti	22	47·90
Lanthanum	La	57	138·92	Uranium	U	92	238·07
Lead	Pb	82	207·21	Vanadium	V	23	50·95
Lithium	Li	3	6·940	Tungsten	W	74	183·86
Lutetium	Lu	71	174·99	Xenon	Xe	54	131·3
Magnesium	Mg	12	24·32	Ytterbium	Yb	70	173·04
Manganese	Mn	25	54·94	Yttrium	Y	39	88·92
Mercury	Hg	80	200·61	Zinc	Zn	30	65·38
Molybdenum	Mo	42	95·95	Zirconium	Zr	40	91·22

GROUP—A

(General and Physical Chemistry)

CHAPTER I

INTRODUCTION

1.1. Space, Matter and Energy. In our daily life, we come in contact with numerous objects—buildings, vehicles, rocks, sands, glass, chalk, milk, rice, wheat, animals and human beings. The objects differ from each other in size, colour, shape and other properties (characteristics). These characteristics of objects can be perceived by one or more of our senses such as touch, hearing, sight, smell and taste. We can recognise by our senses that the objects occupy a certain amount of room which is called space. We also recognise that the two objects cannot occupy the same space at the same time. When an object is removed, we feel that an emptiness is left. *The emptiness that remains when an object is removed is called space.* Therefore, one of the most useful purposes of space is that it can be occupied by objects.

Each of these objects is said to be composed of matter and each differs from the other in a number of ways. But all objects have some weight and occupy some space. Then we may think *matter as anything that occupies space and has weight.* Matter should not to be conceived as something in a state of rest ; something unchanging in reference to position, form and state. It is continually undergoing change. The basic cause for this change is assigned to something which is called energy. *Energy is generally defined as the ability to do work (i.e., the ability to change or move matter).*

1.2. Kinds of matter. Matter exists in an almost infinite variety—it ranges from the lightest gas to the heaviest metal, dynamic living thing like man to lifeless rocks and minerals. The chemist is primarily interested in the study of the nature of this vast variety of matter. Any kind of matter may be referred to as material. Thus wood is material, sugar is another material. A material may be homogeneous or heterogeneous.

A homogeneous material is a material every part of which is identical with every other parts. A few examples of homogeneous materials are sugar, iron and water.

A material which is characterised by the dissimilarity of their parts, i.e., every part of which is not similar with every other parts, is said to be heterogeneous. Some examples of heterogeneous materials are soil, milk, eggs and fruits.

A heterogeneous material is called a mixture. Thus a mixture of two or more homogeneous materials constitute a heterogeneous material. For example, the rock "granite" is a heterogeneous material. This rock is made up of three homogeneous materials, quartz, mica and feldspar.

1.3. Substances. *A substance is a homogeneous material that has fixed composition and fixed properties.* It possesses constant physical properties under specific conditions. Examples of substances are iron, water, sulphur, sugar and salt.

A solution is also a homogeneous material but it has no fixed composition and fixed properties. Thus when sugar is dissolved in a given amount of water, we get a solution. The amount of sugar present in the solution can be varied. Thus the solution is not of definite composition and hence it is not a substance.

1.4. The properties of substances. The characteristics that describe a substance and permit its distinction from other substances are called its properties. For example, an examination on the substance, sugar reveals that it is a solid, that it is crystalline and colourless, tastes sweet, and dissolves readily in water. Each of these is a property of sugar and aids in its identification. Properties are classified usually under two main headings—physical and chemical.

Physical properties. The physical properties are those characteristics of the substances which can be detected by physical senses. These properties can be observed without changing the substance into other substances.

Thus colour of a substance is easily detectable by our physical sense, viz., vision. So colour is a physical property of a substance. Similarly, odour, taste, hardness, melting point, boiling point, transparency, lustre and crystalline structure are some of the physical properties.

The malleability of a substance—the ease with which the substance can be hammered out into thin sheets is also the physical property. The ductility—the ease with which the substance is drawn into wire is another physical property of a substance.

The physical property is further divided into two classes—(i) The intensive physical property and (ii) extensive physical property.

The intensive or specific physical properties are those which are inherent in a substance and are exhibited by all specimens of it. These properties of a substance make its identification and distinctions from other substances. Melting point, boiling point, crystalline structure are some examples of intensive physical property.

The extensive physical properties are those physical characteristics which are not exhibited by all specimens of a given substance. These properties depend upon the quantity of material present in a particular specimen. For example, volume is an extensive property. All specimens of water will not occupy the same volume. This will depend upon the quantity of water present in a particular specimen. Size, shape and weight are other examples of extensive physical properties. It may be noted that the ratio of two extensive properties, mass to volume, is itself a specific property, i.e., density.

It can be said safely that there are not two different substances in the universe which have completely identical properties. Indeed if such were the case they could not be distinguished from each other and would be considered to be the same substance.

The chemical properties. Substances may also be characterised by other class of properties known as the chemical properties. These involve the transformation from one substance to another known as the chemical change. Thus, when a piece of iron is left to moist air it rusts, while gold does not. Thus a new substance, rust is obtained from another substance, iron. The process is described by saying that iron reacts with moist air to form a new substance, rust. One may distinguish gold from iron in terms of their reaction with moist air.

Similarly, if carbon is burned in oxygen, a new substance, carbon dioxide is formed. Thus carbon has entered into a chemical reaction with oxygen in which it is converted into a new substance, carbon dioxide.

The processes that convert substances into other substances are known as chemical reactions.

Chemical properties may be defined as the properties of a substance that relate to its participation in chemical reactions.

Occasionally, the physical properties alone do not suffice to establish beyond reasonable doubt the identity of a given substance. In such cases the chemical properties may confirm the identification. It may be noted here that the primary business of the chemists is the accurate establishment of the chemical properties of the substance.

1.5. Conditions. In addition to physical and chemical properties, there are certain physical attributes which a given sample of matter may possess. Let a quantity of a gas be enclosed in a vessel fitted with piston. When the pressure on the piston is $\mathbf{P_1}$ (fig. 1.1) the gas occupies the volume V_1 ; when the pressure is increased from P_1 to P_2 the piston is lowered and the gas occupies a lesser volume V_2. Thus increasing or decreasing the pressure, we can decrease or increase the volume of the gas. Thus pressure is an attribute and is called condition. Again water is liquid at 30°C but at 0°C it exists as solids. Thus certain properties of water is dependent on temperature. Hence temperature is a condition under which a given quantity of water exists. One must specify the condition that below a certain temperature water exists as solid. Dilution, motion and electrical charge are other examples of conditions.

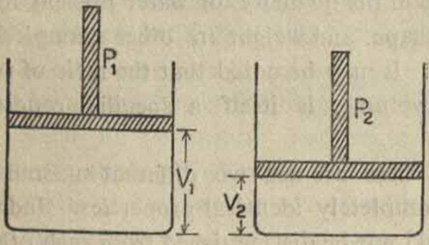

Fig. 1.1

Conditions are the variable attributes which are not concerned with the quantity and not inherent in the substance under consideration but have a marked influence upon some properties. So it is necessary to describe those properties as having been determined under certain conditions.

1.6. Pure substances. Substances are never found pure in nature. The concept "pure substance" is an idealisation ; all actual substances are more or less impure. Thus the substance water has its own properties, but spring water, sea water and distilled water show certain differences in their properties. These differences are due to the presence of other substances called impurities which water has dissolved from its surroundings. These impurities which are present in sea water are sodium chloride, magnesium chloride, etc. Hence sea water is a mixture. When any one substance predominates in a mixture, the whole mixture is called by its name and the other constituents are called impurities. If the impurities are present in very small amount, then the properties of the various specimens of the substance are nearly the same and these properties are accepted as the properties of the ideal substance.

1.7. Changes of substances. It has been pointed out that the substances are continually undergoing change. Two kinds of changes are recognised. These are the physical changes and the chemical changes.

Physical changes. When liquid water is cooled, it becomes ice and when it is heated, it is converted into steam. With this change of condition there have been a few changes in the physical properties of water. This change in condition again does not bring about the formation of a new substance because the matter which makes steam and ice is the same in kind as that of liquid water. When a lead bullet, fired from a riffle, hits a stone, it grows so hot that the lead melts and becomes a liquid. In this case, the composition of initial and final substance is the same, i.e., no new substance is formed. Again, the substances may change their volume by expansion or contraction, they may change their magnetic qualities, as a piece of soft iron in contact with a magnet, attracts other pieces of iron. Such changes are known as physical changes. Such a change brings about a temporary alteration of a few of the physical properties of the substance. The substance regains their original property when the original conditions are re-established.

A physical change is a change which cause an alteration in the properties of a substance without the formation of a new substance.

Chemical changes. When lead is heated for a long time in presence of air, lead is converted into lead oxide (litharge). When magnesium metal is heated in air, a white powder is formed. In both the cases the action of heat furnishes forms of matter with very different specific properties from those forms of matter employed at the start. In other words, in all these changes new substance or substances are produced from the initial substance.

Again, if some zinc granules are placed in a container of hydrochloric acid, bubbles of gas are evolved. If the granules are kept in acid for some time, the evolution of gas will continue, the granules will decrease in size or disappear altogether. Evaporation of the liquid will yield white crystals, while the evaporation of pure acid used leaves no residue. Apparently, therefore, the matter of which zinc granules are composed has disappeared while the matter of which the white crystals are composed has appeared in its place. The properties of the two substances, the zinc granules and white crystals are entirely different. Thus zinc granules have been converted into the new substance, white crystals.

The above examples illustrating the conversion of one substance into other are the examples of chemical changes.

A chemical change is a change which results in a permanent alteration in the properties of a substance with the formation of one or more new substances.

Phenomena which bring about a radical change of substances in which new substances are produced from the initial ones are known as chemical phenomena or chemical reactions, or simply reactions. The substances which enter into a reaction are called reactants while the substances which are formed as a result of the reaction are called products.

1.8. Energy changes in chemical reactions. Chemical reactions are invariably accompanied by energy changes. *Energy is defined as the capacity to perform work.* We recognise energy in many different forms such as kinetic energy, potential energy, electrical energy, heat energy, etc. Most often, the energy changes that accompany chemical reactions involve the liberation or absorption of heat. Some reactions can occur with the evolution of light.

Exothermic reactions. *Chemical reactions in which heat is liberated are called exothermic reactions.* When a compound is formed from simple substances with evolution of heat, it is called an exothermic compound. For example, carbon dioxide is formed from its elements, carbon and oxygen with evolution of heat. Hence, carbon dioxide is an exothermic compound. Other examples of exothermic compounds are water, hydrochloric acid, etc.

Endothermic reactions. *Chemical reactions in which heat is absorbed are called endothermic reactions.* Compounds which are formed from simple substances with the absorption of heat are called *endothermic compounds.* For example, when vapours of sulphur are passed over red-hot charcoal, the compounds, carbon disulphide CS_2, is formed. This reaction is accompanied by the absorption of heat. Hence, carbon disulphide is an endothermic compound. Other examples of endothermic compounds are nitric oxide, hydriodic acid, etc.

Since heat is evolved in an exothermic reaction, these reactions will be favoured at low temperatures. The energy contained in an exothermic compound is less in comparison with simple substances from which they are formed. Hence, the exothermic reactions tend to occur more readily and the products are more stable than the reactants. Endothermic reactions, on the other hand, will be favoured at high temperatures since heat must be supplied for the absorption by the endothermic compound. Naturally, endothermic compounds contain more energy in comparison with simple substances from which they are formed. Hence, the products of endothermic reaction will be less stable than the reactants.

Any reaction that is exothermic when it occurs in one direction, is endothermic when it takes place in the reverse direction.

For example, when the reaction between hydrogen and iodine proceeds in the forward direction { from left to right of the equation which means the combination of hydrogen and iodine },

$$H_2+I_2\rightleftarrows 2HI$$

absorption of heat takes place. When this reaction takes place in the reverse direction { from right to left which means the decomposition of hydriodic acid, $2HI\leftrightarrows H_2+I_2$}, evolution of heat takes place.

Energy and its classification. Energy was defined earlier as the capacity for doing work. All chemical changes are accompanied by energy changes. Heat, light and electrical energy are common types of energy involved. These energy changes indicate that both reactants and products in a chemical reaction must contain energy. *Internal energy is defined as the quantity of energy* *that a substance possesses as a result of its characteristic chemical composition and temperature.*

Kinetic energy is the energy which a substance has because of its motion. The quantity of the kinetic energy possessed by a given substance is dependent upon both the mass and the velocity of the substance and is given by the formula :

$$K.\,E = \frac{1}{2}mv^2$$

where *m* is the mass of the substance and *v* is the velocity.

Potential energy is the energy due to position. A stone raised above the surface of the earth possesses potential energy. In falling, it can do work.

1.9. Law of conservation of energy. It has been established by careful investigations that *energy can be neither created nor destroyed.* In any physical or chemical change, energy is conserved. However, energy may be converted from one kind to another. Whenever energy of one kind disappears, an equivalent amount of energy of other kinds is produced. This principle is called the law of conservation of energy.

A rock resting on a precipice has potential energy. If it falls over the edge, its potential energy is changed into the kinetic energy. During its fall, its potential energy at any point has decreased by an amount just equal to its gain in kinetic energy. If the rock is raised to its original position, its initial value of potential energy will be restored.

When a piece of iron is pounded with a hammer, it becomes hot ; in this process the kinetic energy is converted into the thermal energy. When electricity is passed through a filament into a light bulb, we get light and the bulb becomes heated. In this process, the electrical energy is converted into light and thermal energy. In all these changes, energy has been neither created nor destroyed but merely changed from one form into another.

Whether a chemical change will occur spontaneously, can be interpreted from the viewpoint of energy. Suppose you have a stone in your hand and let it go. It falls on the ground. The stone at a higher level possesses more potential energy than does the stone on the ground. In the process of falling, the stone, therefore, goes from the state of higher energy to the state of lower energy. The occurrence of any spontaneous change is a manifestation of the tendency of all chemical substances to exist in the lowest possible energy state. There is a relationship between this tendency and stability of chemical substances. The condition of lowest energy corresponds to the state of greatest stability. The higher is the energy of a substance in a particular state, less stable the substance is in that state.

With this viewpoint we can predict the direction in which a chemical reaction will proceed. This will depend on whether the "reactants" or "products" exist in a state of lower energy. If the reactants exist in a state of higher energy, a chemical reaction will proceed spontaneously to form products. The products of such reactions (exothermic) are more stable than the reactants. On the other hand, if the reactants exist in a state of lower energy, the reaction will not proceed spontaneously. Energy (i.e., heat) must be supplied to the reactants in order to make the reaction occur. Since energy is absorbed during the occurrence of such reactions (endothermic), the products are in a state of higher energy than the reactants. Hence, the products of such a reaction (endothermic) are less stable than the original reactants.

For example, we can speculate the direction in which the chemical reaction represented by $A+B=AB$ will proceed. If the sum of internal energies of the substances A and B is higher (they are in a state of higher energy) than that of the product AB (the product is in a state of lower energy) the reaction will proceed spontaneously from left to right. Since in any chemical process, energy is neither created nor destroyed, heat will be evolved in this reaction. The same amount of heat must be absorbed when the reaction proceeds in the reverse direction. An example is the burning of carbon

$$C+O_2=CO_2$$

This reaction liberates 94,040 calories of heat. For this reaction we can write :

$$(\text{internal energy of carbon}+\text{internal energy of oxygen}) - (\text{internal energy of carbon dioxide})=94{,}040 \text{ cals.}$$

When this reaction proceeds from right to left, i.e., the decomposition of carbon dioxide into carbon and oxygen, 94,040 calories of heat will be absorbed.

On the other hand, when sum of the internal energies of A and B is less than that of the product, the reaction will not proceed spontaneously from left to right ; heat must be supplied to cause the reaction. In this case, the product AB is in a state of higher energy than the reactants. The reaction of carbon and sulphur to form carbon disulphide is an example. This reaction can be written as

$$C+2S=CS_2$$

This reaction absorbs 25,400 calories of heat. Hence, carbon disulphide is in a state of higher energy than the reactants, carbon and sulphur. When this reaction proceeds in the reverse direction, i.e., the decomposition of carbon disulphide into carbon and S, exactly 25,400 calories of heat will be evolved according to the law of conservation of energy.

1.10. The Science of Chemistry. We are now in a position to understand what chemistry is. *The science that treats of chemical phenomena is called chemistry.* Hence chemistry is the science of the transformation of substances. It studies the composition and properties of substances, the relation between the properties of substances and their composition, the conditions and ways of changing substances into one another.

When changes in substances occur, there are accompanying energy changes, Thus heat energy is evolved when wood and coal change into gases and ashes. This heat energy is used in our home for cooking food and to provide power for industry. Hence chemistry cannot ignore the energy changes which occur in the changes of subtances.

Finally, we may say that the science of chemistry is concerned principally with substance and energy. Summarisingly we can state that chemistry deals with :

(i) The composition and properties of substance. For example, water is composed of hydrogen and oxygen. When liquid water is cooled, it is converted into ice. This is the property of the liquid water.

(ii) The changes of substances into one another. The rusting of iron is an example.

(iii) The causes that bring about changes in substance. The presence of moisture in the air is the cause for rusting of iron.

(iv) The energy changes that accompany the transformations of substances. Petrol burns with the liberation of vast amount of heat energy.

(v) The laws that govern the changes of the substances.

Since the changes which substance will undergo are of primary importance to the chemists, the understanding of these changes in terms of submicroscopic particles of which substances are composed becomes very essential to the chemists.

1.11 Division of Chemistry. Chemical changes are often accompanied by physical changes. Numerous chemical changes occur in the biological system. Continuous chemical changes take place in the organisms by a continuous exchange of substances between the organisms and its surroundings (metabolism). In order to study the numerous chemical changes conveniently, it is necessary to subdivide chemistry into different branches. The branches of chemistry are : (1) Physical chemistry, (2) Organic chemistry, (3) Inorganic chemistry, (4) Analytical chemistry, (5) Biochemistry and (6) Industrial chemistry.

Physical Chemistry. Physical chemistry deals with the fundamental principles upon which all other phases of chemistry are based. So it is the investigation of laws and theories of the science of chemistry. The laws and theories then serve to explain the facts which we observe. Physical chemistry is also the search of knowledge of the fundamental structure of matter and with the help of this knowledge, the transformations of substances into one another are explained. In a sense, physical chemistry bridges the gap between physics and chemistry and is characterised by description in the language of mathematics.

Analytical Chemistry. It deals with the separation, identification and composition of various kinds of matter. The analysis of a particular sample of matter is of two kinds. The qualitative analysis provides method to find out what is present in a particular sample of matter. The quantitative analysis, on the other hand, provides methods to find out how much of each constituent is present.

Analytical chemistry is the most important branch of chemistry. Without its help little could be accomplished in any branch of chemistry.

Organic Chemistry. It is the chemistry of carbon compounds and mainly deals with the substances of plant and animal origin, viz., fats, oils, proteins, carbohydrates, vitamins, etc. An important part of organic chemistry is that of synthesis. Synthesis is the process of forming complex compounds from relatively simple starting materials.

Inorganic Chemistry. It mainly deals with the elements other than carbon and their compounds. Study of minerals, ores, radioactivity, metal, alloys, acid, bases, salts, etc., come under the scope of inorganic chemistry.

Biochemistry. It bridges the gap between chemistry and biology and mainly deals with the chemical changes that take place in living organisms. The mechanisms by which living cells synthesize specific protein molecules which are processes basic to life are studied under this head. The study of antibiotics, vitamins, hormones, etc., come under the realm of biochemistry.

The synthesis and study of medicines come under a specialised branch of Biochemistry known as Pharmaceutical chemistry.

Industrial Chemistry. It is concerned with the application of chemistry to industry and deals with the development of chemical processes for the production of useful products on large scale. The manufacture of soaps, cement, paper, paint, varnishes, dyes, plastics, drugs, alloys, perfumes, rubber, fibres, oils, fats, sugar, explosives, and abrasives, etc., come under the realm of industrial chemistry.

In addition to these branches of chemistry there are several other specialized branches of chemistry which are given special names such as agricultural chemistry, high polymer chemistry, physiological chemistry, mineral chemistry, photochemistry, radiation chemistry, electrochemistry, etc. As the study of the science of chemistry progresses, the connotations of these terms will become increasingly obvious.

1.12. The Experiment. Chemistry is largely an experimental science. In chemistry, the study of any phenomenon begins first of all with observation and description of the phenomenon. The next step is to explain the observed phenomenon. In order to explain them it is necessary to ascertain their causes, to establish under which conditions they occur in nature. For this purpose, various phenomena are artificially reproduced in the laboratory under conditions and in an environment which are most suitable for their study. *The artificial reproduction of a phenomenon is known as an experiment.* In nature, phenomena are often so masked by other conditions that they cannot be accurately observed unless the obscuring conditions are suppressed. By experiment it is possible to eliminate such complex disturbing and obscuring conditions so that a phenomenon is accurately studied. When the results of the study of phenomenon are recorded, they are called "data".

Let us take an example. We know that water evaporates and is converted into steam. The steam, when cooled is again converted into liquid water. The raining is the cause of condensation of water vapours which are formed by evaporation of sea water. Thus evaporation and condensation of water are very well known phenomena of nature. These phenomena may be artificially reproduced in the laboratory as follows :

A flask containing water is fitted with a condenser through which cold water is made to circulate. The flask is then heated and the vapour formed passes through the condenser where it is cooled and converted into liquid water. This water is collected into another flask called the receiver. The operation as a whole is called an experiment.

1.13. The scientific method. The scientific method is a technique of investigation of phenomena of nature and is applicable in every field of science. The proper use of scientific method involves four distinct operations. The first step is the accumulation of data. These data may be obtained by the observation of both naturally occurring phenomena and carefully planned and executed experiments. The second step is the collation and grouping of data. From this grouping of data it is frequently possible to develop generalisations concerning some particular behaviour of nature under certain specified conditions. Such reasoning which leads to generalisations from the specific is called *induction.* In the third step, attempts are made to develop a suitable explanation of the described behaviour of the phenomena. The explanation which becomes compatible with all of the known data is accepted as the proper one.

In the fourth step, it is often possible to predict what should be the results of certain experiments which has not yet been tried. This prediction is based on the considerations of the explanation developed in the third step. Therefore, by performing these experiments, it is possible to check the validity of the explanation offered in the third step. If the results of these experiments are not compatible with the predicted results, a new explanation must be evolved. In this step specific results are predicted from the general considerations. Such reasoning which is from general to the specific is called *deduction.*

The correlation of data requires qualities of the mind different from those employed in observation and experiment. Both qualities are not always located in the same individual. So all the four steps are not necessarily taken by the same individual nor the steps are always taken immediately after each other. The facts may have been gathered by a talented experimentalist long before, but their interpretation may have had to await the advent of an individual particularly brilliant in the work of correlation.

1.14. Laws, Hypotheses and Theories.

Laws. When a large number of observations concerning some certain behaviour of nature have been made, it is necessary to summarise the findings in a general statement. *Such a general statement which includes within itself a number of facts is called a law.* The law is a generalisation which does not extend beyond the observed facts. A law is thus limited by the facts it describes. Thus Boyle's observations on gases (see Boyle's law) can be condensed into one brief sentence which describes how gases behave when their pressure is changed. This brief sentence is known as Boyle's law.

Such laws are the result of the application of the second step of the scientific method.

Hypotheses. After the law has been established, the next concern is to find the causes of many phenomena occurring in nature. For this reason, scientists are compelled to make ideas or assumptions. Assumption put forth to explain a phenomenon, to establish its connection with other phenomena studied earlier, to unite several phenomena under common ideas is called a hypothesis.

The development of the hypothesis is the third step of the scientific method.

Theories. If the conclusions which follow logically from the hypothesis are confirmed by experiment, if the hypothesis explains not only the phenomenon in question, but permits general conclusions and prediction of new phenomenon as well, the hypothesis is dignified by the name of the theory. If the deductions that are made from the hypothesis does not agree with the results of the experiments the hypothesis must be discarded.

The Greek philosophers had developed the hypothesis that all matter is made up of tiny particles which they called atoms. They were not experimentalists and did nothing to test the validity of their proposal, yet all observations made later, confirm this idea. Today we call this "The Atomic theory".

Theory explains the observed laws. Thus kinetic molecular theory explains Boyle's, Charles', Dalton's and other laws of gases.

APPENDIX I

Distinction between physical and chemical changes.

Physical change	Chemical change
(1) Only physical properties of the substance are altered.	Both physical and chemical properties of the substance are altered.
(2) The composition of the substance remains unaltered.	The composition of the substance is altered giving new substance.
(3) No new substance is formed.	New substance or substances are always formed.
(4) Change is usually temporary.	Change is permanent.
(5) It is not usually accompanied by marked evolution or absorption of heat (except that the latent heat is absorbed in the change of state).	It is always accompanied by either absorption or evolution of heat.

Physical change	Chemical change
(6) The substance regains its original property when the initial conditions are re-established.	The substance cannot regain its original property when the initial conditions are re-established, i.e., the new substance formed cannot be converted into the original substance by re-establishing the initial conditions.
(7) The weight of a substance remains unaltered.	The weight of the substance usually alters when it is transformed into new substance or substances.

EXERCISE

1. Define the following : (a) matter, (b) homogeneous material, (c) heterogeneous material & (d) substance.
2. Distinguish between materials and substances. Which of the following varieties of matter are substances and which only materials ?

meat	gold	bread	silver
potato	water	iron	brass
tomato	granite	calcite	milk
sugar	wood	table salt	aluminium

3. Define the following : (a) property, (b) physical property, (c) chemical property and (d) condition.
4. Distinguish between "specific" and "extensive" physical property ; "extensive physical property" and "condition". Are colour, odour and taste specific physical properties ?
5. Explain clearly what you understand by the physical and chemical changes. Give examples.
6. Define chemical reaction. What do you mean by reactant and product.
7. Which of the following are physical changes and which are chemical changes.

   (a) Dissolving of sugar into water, (b) rusting of iron, (c) corrosion of iron, (d) burning of candle, (e) burning of petroleum, (f) formation of snow, (g) heating of platinum wire, (h) compression of air.
8. Define chemistry. How does organic chemistry differ from inorganic chemistry ? What areas of knowledge are interlinked in (a) bio-chemistry and (b) physical chemistry.

9. What is meant by the "scientific method". Distinguish among "law", "hypothesis" and "theory". Which of these is most likely to undergo modification ? Explain.
10. Define "Experiment". Describe an experimentation of a phenomenon commonly observed in nature.
11. What steps are involved in the application of the scientific method ?
12. "Nature speaks to us in a peculiar language, the language of phenomena ; she answers all the questions we ask her and these questions are our experiments"—Justify the statement.
13. What do you mean by energy ? State the law of conservation of energy.
14. Explain the law of conservation of energy.

CHAPTER II

THE COMPOSITION OF MATTER

2.1. The chemical elements. As we look about us, we find many recognisably different kinds of matter. The ancient Greek philosophers who knew far fewer types of matter than does modern man, came to the conclusion that all matter is made up of a relatively few simpler types just as different structures may be made from steel, bricks, and mortar. This basic idea of the composition of matter was sound and has been substantiated fully by the work of many experimentalists. The extensive experimental work of many scientists has confirmed that there are fewer than one hundred different basic components of matter. These basic components are called the elements. Everything on this earth, e.g., sugar, salt, wood, man, etc., is composed only of one or more of these elementary substances and nothing else.

Elements or elementary substances may be defined as those substances which cannot be broken down into simpler chemical substances by chemical means. The inclusion of the term "by chemical means" into the definition is essential because there are certain elements which undergo changes spontaneously. As a result of such spontaneous change, new elements are formed from the parent element. At present, 98 of these simple and fundamental varieties of matter are known. Hundreds of thousands of materials arise from their interaction.

2.2. Symbols. The chemist for the sake of convenience uses a shorthand system or symbols which stand for the names of the elements. The idea seems to have originated with the alchemists. Alchemists kept records of their work in private codes in order to prevent discovery by others of the secrets which they had deciphered. Because there was no general system of symbols, much confusion resulted when one chemist consulted the writings of the other. Some of the symbols used by alchemists are given in fig. 2.1.

In 1811 the Swedish chemist Barzellius proposed the present system of chemical notation. According to this notation, the first letter of the name of the element is used to represent it. Thus, H is the symbol for hydrogen ; O for oxygen ; C for carbon and N for nitrogen. When more than one element have the same initial letter, the initial letter and another letter are used. Thus, calcium, carbon and chlorine have the same initial letter C but their symbols are respectively Ca, C and Cl. The symbols of some chemical elements are derived from the latin name of the elements. For example, sodium is represented by Na (latin name is Natrium) silver by Ag (latin name—Argentum), Mercury by Hg (Latin name—Hydrargyrum), potassium by K (Lat—Kalium), copper by Cu (Lat—Cuprum), Tin by Sn (Lat—Stannum), Iron by Fe (Lat—Ferrum), etc.

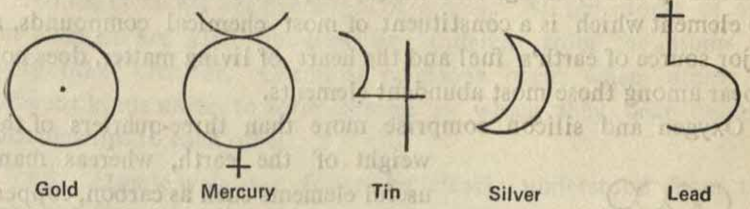

Fig. 2.1

By modern convention, a symbol stands not only for the name of the element but also for one atom of the element or atomic weight of the element. Thus O not only stands for oxygen, but also represents one atom of oxygen and also 16 parts by weight of oxygen. Similarly, C means one atom of carbon and 12 parts by weight of carbon.

2.3. The distribution of the elements. It would be interesting to know how the different elements are distributed throughout the earth and the universe.

Of the 98 elements, only about twenty are found in nature in an uncombined condition, whereas the rest occurs in combined state. The elements are not distributed equally in nature. Table 2.1 lists the relative quantities of the ten most abundant elements in earth's crust, in the seas and in the atmosphere.

TABLE—2.1

Element	Per cent	Element	Per cent
Oxygen	49.2	Sodium	2.6
Silicon	25.7	Potassium	2.4
Aluminium	7.4	Magnesium	1.9
Iron	4.7	Hydrogen	0.9
Calcium	3.4	Titanium	0.6

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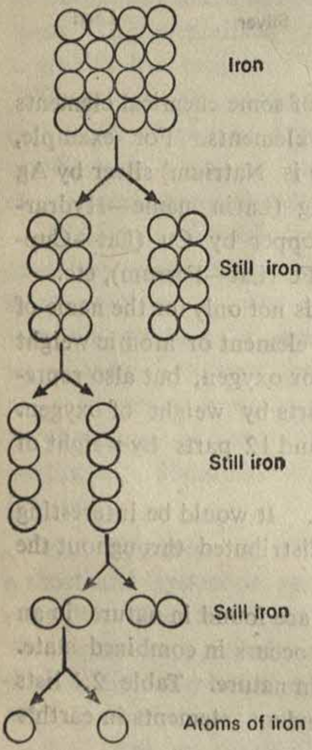
These ten elements account for almost 99% of the earth's crust and atmosphere. The remaining elements may be considered as almost impurities, though exceedingly important ones. Thus, carbon, the element which is a constituent of most chemical compounds, a major source of earth's fuel and the heart of living matter, does not appear among those most abundant elements.

Oxygen and silicon comprise more than three-quarters of the weight of the earth, whereas many useful elements such as carbon, copper, gold, lead, sulphur, tin, etc., together make up slightly more than 1% of the total.



At this stage further subdivision would be much more difficult and would give subatomic particles such as electron, proton, neutron, etc.

Fig. 2.2

2.4. Atom. Since elements are the fundamental varieties of matter, and all materials arise from their interaction, we must have a clear understanding about the nature of the element. Let us take a piece of an element, iron, for an example. If we would cut this into two, each part would still be iron. If we could thus go on subdividing it indefinitely, we would finally reach a point at which further subdivision would be much more difficult. After this point, if we further divide it by special methods, we would get no longer iron but instead, unstable particles known as subatomic particles. These particles are very difficult to characterise. In this way, if the piece of iron were separated into the smallest possible segments which are still iron, it would be found that all the segments are identical particles. These particles are the basic building blocks of iron and are called atoms of iron.

An atom is the smallest particle of an element which can enter *into a chemical reaction*. It is the fundamental unit of which the element is built.

All the elements are composed of atoms. All the atoms of any one element are alike but they are different from the atoms of every other element. Chemical reactions occur when atoms of different kinds unite to form groups in which they bear definite relationships to each other.

2.5. Atomic weights. It can be clearly understood from the previous discussion that the atoms of the elements are so small that they are invisible and that there is no possibility of weighing a single atom of elements and thus establishing a scale of atomic weights. However, chemists have evolved an extremely useful relative weight scale for the elements called the atomic weight scale. This is a set of numbers that expresses relative weights of different kinds of atoms. In order to do this, the weight of one atom of an element is taken as the standard and then the weight of one atom of other elements is determined relative to that of an atom of the standard element. Hence,

$$\text{Atomic weight of an element} = \frac{\text{Weight of one atom of the element}}{\text{Weight of one atom of the standard element}}.$$

Thus the atomic weight is a ratio and has no unit. It does not give the actual weight of an atom of the element.

Hydrogen is the lightest of the elements. For this reason, Dalton determined the atomic weight of the elements taking the weight of one atom of hydrogen as 1 (hydrogen scale). Therefore, on hydrogen scale the atomic weight is defined as :

The atomic weight of an element is a number which shows how many times an atom of the element is heavier than one atom of hydrogen. On this scale one atom of hydrogen has a weight of 1 unit. That is.

$$\text{Atomic weight of an element} = \frac{\text{Weight of one atom of the element}}{\text{Weight of one atom of hydrogen}}.$$

The atomic weight of nitrogen is 14. This means that one atom of nitrogen is 14 times as heavy as one atom of hydrogen. The atomic weight of chlorine is 35·5. It means that the weight of one atom of chlorine is 35·5 times the weight of one atom of hydrogen.

Subsequently, oxygen was taken as the standard element instead of hydrogen. Taking the weight of one atom of oxygen as 16 (oxygen scale) the atomic weights of other elements have been determined. Therefore, on oxygen scale the atomic weight of an element is defined as follows :

The atomic weight of an element is the weight of one atom of the element as compared with the weight of one atom of oxygen taken to be 16. In other words, on this scale, the atomic weight of an element is a number which shows how many times the weight of one atom of the element is heavier than one sixteenth part of the weight of one atom of oxygen. Therefore,

$$\text{Atomic weight of an element} = \frac{\text{Weight of one atom of the element}}{\text{Weight of one atom of oxygen}/16}$$

or, Atomic weight of an element

$$= \frac{\text{Weight of one atom of the element}}{\text{Weight of one atom of oxygen}} \times 16.$$

On oxygen scale the atomic weight of sodium is 23. This means that an atom of sodium is 23/16 times as heavy as an atom of oxygen.

Reasons for acceptance of oxygen as a standard element. Oxygen is taken as a standard element for the following reasons. (1) oxygen is much more active than hydrogen. Oxygen can combine chemically with almost all the elements. (2) On $O=16$ scale the atomic weights of the elements come to whole numbers or very near to whole numbers. (3) Hydrogen is the lightest of all elements. Hence the experimental error obtained during the determination of atomic weights of the elements taking hydrogen as the standard will be much reduced when oxygen is taken as a standard for comparison.

From 1961, the atomic weights of the elements are determined taking carbon* as the standard element. On this new carbon scale, the atomic weights of the elements are found out by taking the weight of one atom of carbon as 12. *The atomic weight of an element is the weight of one atom of the element as compared with the weight of one atom of carbon taken as 12.* Hence on this scale the atomic weight of an element is a number which represents how many times the weight of one atom of the element is heavier than $\frac{1}{12}$ of the weight of one atom of carbon. Hence,

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*Carbon is a solid element. It has three isotopes, viz.. ${}_6C^{12}$, ${}_6C^{13}$, and ${}_6C^{14}$. Among them ${}_6C^{12}$ is most abundant in nature. On $C=12$ scale, the atomic weights of highest number of elements come to whole numbers. For these reasons, the atomic weights of the elements are determined taking the weight of one atom of carbon as 12.

$$\text{Atomic weight of an element} = \frac{\text{Weight of one atom of the element}}{\text{Weight of one atom of carbon/12}}$$

or, Atomic weight of an element

$$= \frac{\text{Weight of one atom of the element}}{\text{Weight of one atom of carbon}} \times 12.$$

On this scale the atomic weight of phosphorus is 31. This means that one atom of phosphorus is 31/12 times as heavy as one atom of oxygen. On carbon scale the atomic weight of oxygen comes out to be 15·999415 and the atomic weight of hydrogen is 1·0079. Hence the difference between the atomic weights of the elements on the carbon scale and that on the oxygen scale is insignificant

The atomic weight of an element is not the actual or absolute weight of the element. It is only a relative number. Therefore, we can know the relative weights of the elements from the numbers by which the atomic weights of the elements are expressed. For this reason, the atomic weight has no unit.

The atomic weight of an element when expressed in gram is called gram-atomic weight. For example, 35·5 gm is the gram-atomic weight of chlorine. By one gram-atom of chlorine is meant 35·5 gm of chlorine. The unit of gram-atomic weight is gram.

2.6. The absolute weight of atoms. Although the relative weights of atoms are very useful, it is sometimes necessary to know the actual or absolute weight (usually in grams) of a given kind of atom. This is done by resorting to an indirect approach to this problem, because we cannot weigh a single atom of the element. The method consists of finding out the number of oxygen atoms present in 16.0000 grams or the number of hydrogen atoms present in 1.008 grams. Thus, dividing the gram-atomic weights by the number of atoms present in it, we get the absolute weight of a given kind of atom.

Fortunately, the number of atoms in the gram-atomic weight of any element has been measured by several quite independent methods. The most precise value comes out to be 6.023×10^{23}. This is known as the Avogadro's number, in honour of the Italian physicist Amadeo Avogadro and is usually represented by N. We can now calculate the absolute weight of an atom from the gram-atomic weights.

$$\text{The absolute weight of an atom} = \frac{\text{Gram-atomic weight}}{6.023 \times 10^{23}}$$

Thus one single atom of oxygen weighs

$$\frac{16{\cdot}0000}{6.023 \times 10^{23}} = 2.656 \times 10^{-23} \text{ gram.}$$

$$\text{The absolute weight of the hydrogen atom} = \frac{1.008}{6.023 \times 10^{23}}$$
$$= 1.673 \times 10^{-24} \text{ gram.}$$

2.7. The number of atoms present in one gram-atom of an element. It has been mentioned earlier that the number of atoms present in one gram-atomic weight of the elements is the same. This can be proved in the following way :

Let us suppose that,

the atomic weight of an element $= a$

the weight of one atom of the element $= x$ gm.

the weight of one atom of oxygen $= y$ gm.

Therefore, on oxygen scale,

the atomic weight of the element, $a = \dfrac{x}{y/16}$

$$\therefore \quad a = \frac{x}{y} \times 16$$

Now, the absolute weight of one atom of oxygen $= y$ gm.

The number of atoms of ogygen present in 16 gram of oxygen or one gram-atomic weight of oxygen $= \dfrac{16}{y}$.

Again, the absolute weight of one atom of the element $= x$ gram.

$\because$ the number of atoms of the element present in *a* gram of the element or 1 gram-atomic weight of the element

$$=\frac{a}{x}=\frac{x\times 16}{y\times x}=\frac{16}{y}\quad\left[\because\ a=\frac{x\times 16}{y}\right]$$

$$\therefore\ \frac{a}{x}=\frac{16}{y}.$$

Therefore, the number of atoms present in one gram-atom of any element = the number of atoms present in one gram-atom of oxygen.

Hence the number of atoms present in one gram-atom of any element is the same. For example, the same number of atoms ($6{\cdot}023\times 10^{23}$ atoms) are present in 23 grams of sodium, 35·5 grams of chlorine or 1·008 gram of hydrogen. If *a* is the atomic weight of an element, then the number of gram-atoms (*n*) present in *g* grams of the element is given by

$$n=\frac{g\text{ gram}}{a\text{ gram}}=\frac{g}{a}.$$

Hence, the number of gram-atoms

$$=\frac{\text{Weight of the element in gram}}{\text{Atomic weight of the element}}.$$

Atomic mass unit (amu). The masses of atoms are expressed on atomic weight scale, i.e., on a scale on which the carbon atom has a weight of 12 units. Unit mass on this scale is referred to as ***atomic mass unit.***

Now the mass of any atom in grams is equal to its atomic weight divided by Avogadro number. Hence an atomic mass unit *(amu)* is equivalent to $\frac{1}{6{\cdot}023\times 10^{23}}=1{\cdot}6603\times 10^{-24}$ gm.

Mass of a carbon atom $=\frac{12}{6{\cdot}023\times 10^{23}}$ gm.

Mass of a oxygen atom $=\frac{16}{6{\cdot}023\times 10^{23}}$ gm.

Hence, 1 *amu* $=\frac{1}{6{\cdot}023\times 10^{23}}=1{\cdot}6603\times 10^{-24}$ gm

$=\frac{1}{12}$th of the mass of a carbon atom

$=\frac{1}{16}$th of the mass of a oxygen atom.

Mass of a hydrogen atom $= 1{\cdot}008$ amu

$$= 1{\cdot}008 \times 1{\cdot}6603 \times 10^{-24} \text{ gm}$$

$$= 1{\cdot}673 \times 10^{-24} \text{ gm.}$$

Similarly, the mass of a nitrogen atom $= 17$ amu

$$= 17 \times 1{\cdot}6603 \times 10^{-24} \text{ gm.}$$

$$= 28{\cdot}2251 \times 10^{-24} \text{ gm.}$$

2.8. Compounds and Molecules. The differences between elements and other substances can now be understood. All other substances are made by the combination of different elements and by mixtures of such combinations. Such combinations in which the individual elements have lost their properties and entirely new properties appear, are called chemical compounds. Then the following are the differences between elements and compounds :

(i) Elements consist of only one kind of atom, whereas compounds always contain two or more kinds of atom.

(ii) In chemical combination, the properties of the component elements have entirely disappeared and new properties characteristic of the compound appear.

(iii) A compound can be decomposed into two or more simpler substances, whereas element does not undergo decomposition into substances simpler than the element.

(iv) When any element is freed from combination with other elements, it regains completely its original properties.

Thus, the loss of property of the element incurred when it forms compound with other elements, does not actually signify the destruction of the element.

A compound may be defined as a substance which is formed as a result of chemical combination of two or more elements and consequently a compound can be broken down into two or more elements.

From the above discussions it is now clear that atoms are the fundamental building blocks of the elements. Similarly, a compound is built up of smallest particles characteristic of that compound. These tiniest particles (or building blocks of compound) are called molecules. Thus, *a molecule is a chemical* *combination of two or more atoms, and is the smallest possible sample of the compound.* If the molecule is broken down further, it is changed into atoms or smaller groups of atoms, having different properties. The molecules of a specific compound are identical in every respect, molecules of different compounds are different. Now we can define a molecule as :

A molecule is the smallest particle of a substance (element or compound) which is capable of independent existence and possesses the chemical properties of that substance. A molecule of individual elements may be formed as a result of combination of atoms of the same kind. For example, two atoms of hydrogen combine with each other to give a molecule of hydrogen. Similarly, molecules of oxygen, nitrogen and chlorine are composed of two atoms of oxygen, nitrogen and chlorine respectively. These are called diatomic molecules. Most of the elements exist as monatomic molecules, that is, a molecule consisting of one atom. A molecule of an element contains atoms of the same kind. A compound contains molecules which are composed of at least two different kinds of atoms.

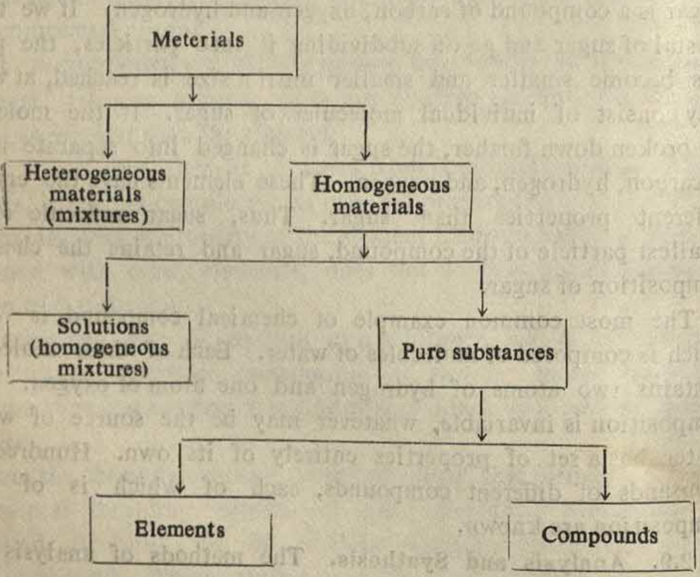
The above statement can be further clarified by illustrations. Sugar is a compound of carbon, oxygen and hydrogen. If we take a crystal of sugar and go on subdividing it into particles, the particles become smaller and smaller until a size is reached, at which they consist of individual molecules of sugar. If the molecules are broken down further, the sugar is changed into separate atoms of carbon, hydrogen, and oxygen. These elements have the entirely different properties than sugar. Thus, sugar molecule is the smallest particle of the compound, sugar and retains the chemical composition of sugar.

The most common example of chemical compound is water which is composed of molecules of water. Each of these molecules contains two atoms of hydrogen and one atom of oxygen. This composition is invariable, whatever may be the source of water. Water has a set of properties entirely of its own. Hundreds of thousands of different compounds, each of which is of fixed composition are known.

2.9. Analysis and Synthesis. The methods of analysis and synthesis enable one to determine the composition of mixtures, solutions and compounds. Analysis is a destructive process which brings about a separation of mixtures and solutions and decomposition of a compound into two or more simpler substances. The reverse process is the synthesis which is a process of building up a substance by combining two or more substances. The composition of a compound can be determined by analysis. Analysis is divided into a number of branches of which two are worth mentioning here : (i) Qualitative analysis and (ii) Quantitative analysis.

Qualitative analysis is used to identify the components or constituents of the mixtures or compounds. For example, a qualitative analysis of sodium chloride can be carried out by decomposing it with electric current and identifying the products as sodium and chlorine. Then we can say that the compound, sodium chloride is composed of two elements, sodium and chlorine. To carry out the quantitative analysis, we would have to weigh the substance and could then learn that the compound contains 39.4% sodium and 60.6% chlorine.

2.10. Table of classification of matter. We can now summarise the classification of matter in the following chart :


Meterials
Heterogeneous materials (mixtures)
Homogeneous materials
Solutions (homogeneous mixtures)
Pure substances
Elements
Compounds

2.11. Formulas. Molecules are composed of several atoms which may be of like or unlike nature. Just as symbols are used to represent atoms, formulas are used to represent molecules of both elements and compounds. For example, it is known on the basis of evidences that oxygen molecule consists of two atoms of oxygen. This is represented by writing the symbol for oxygen and appending the right subscript 2, thus O_2 is the formula of oxygen molecule. Most of the common gaseous elements such as hydrogen, nitrogen, chlorine, fluorine and bromine exist in the form of molecules having two atoms per molecule. These are, therefore, represented by H_2, N_2, Cl_2, F_2 and Br_2 respectively.

Compounds are represented by formulas which are made up of the symbols of the elements contained in the compounds. The subscripts are used to the right of the symbols to indicate how many atoms of that particular element are present. Thus the formula for hydrogen chloride which contains one atom of hydrogen and one atom of chlorine per molecule is HCl (the subscript 1 is not usually written in the formula). One molecule of water contains two atoms of hydrogen combined with a single atom of oxygen. A molecule of water is, therefore, represented by the formula H_2O. A molecule of hydrogen peroxide, on the other hand, contains two atoms of hydrogen and two atoms of oxygen. Hence it is represented by the formula H_2O_2.

Sometimes, parentheses are used to indicate how the atoms are grouped together in the molecule. The subscripts are placed to the right of the parentheses. Thus, the formula of magnesium hydroxide is written as $Mg(OH)_2$ which consists of one magnesium atom, two oxygen atoms and two hydrogen atoms. In some compounds, number may appear in front of a group of symbols. For example, the formula of Glauber's salt is $Na_2SO_4, 7H_2O$ which consists of seven molecules of water (fourteen hydrogen atoms and seven oxygen atoms), two atoms of sodium, one atom of sulphur and four atoms of oxygen. *The combination of symbols and subscripts which represents the composition of a molecule is called a chemical formula.*

Ordinary cane sugar chemically known as sucrose is a much more complicated compound than those just mentioned. The formula of sucrose is $C_{12}H_{22}O_{11}$. This formula tells us that each molecule of sucrose contains 12 atoms of carbon, 22 atoms of hydrogen and 11 atoms of oxygen. The same formula of sucrose can be expressed as $H_{22}C_{12}O_{11}$ or $O_{11}C_{12}H_{22}$ or $C_{12}O_{11}H_{22}$. All such formulas represent the same thing and give the same information. But conventionally, sucrose is represented by that formula which is given first.

2.12. Molecular weights and significance of chemical formula. Since atoms combine to form molecules, the relative weights of atoms lead directly to values for the relative weights of molecules. The molecular weight of any compound is simply the sum of the relative weights of all the atoms in one molecule of that compound. For example, the molecular weight of water, H_2O, must be equal to $(2\times 1{\cdot}008+1\times 16)=18.0160$; since 1.0080 is the atomic weight of hydrogen and 16.00 is the atomic weight of oxygen. Similarly, since hydrogen peroxide molecule, H_2O_2, contains two atoms of hydrogen and two atoms of oxygen, the relative weight of this molecule is $(2\times 1.008)+(2\times 16.00)=34.0160$.

Oxygen in the free state is composed of molecules, each of which contains 2 oxygen atoms. It is, therefore, represented by the formula, O_2, and its molecular weight is equal to $2\times 16=32$.

From the above discussion it is obvious that the atomic weight and the molecular weight are fixed on the same scale. Therefore, the molecular weight is defined as follows :

The molecular weight of a substance is the weight of a molecule of the substance compared with the weight of an oxygen atom taken as 16. Hence, Molecular weight of a substance

$$=\frac{\text{Weight of one molecule of the substance}}{\text{Weight of one oxygen atom/16}}$$

or, Molecular weight of a substance

$$=\frac{\text{Weight of one molecule of the substance}}{\text{Weight of one oxygen atom}}\times 16.$$

On the carbon scale the molecular weight is defined as follows :

The molecular weight of a sabstance is the weight of one molecule of the substance compared with the weight of a carbon atom taken as 12. Hence on the carbon scale, the molecular weight of a substance is a number which represents how many times the weight of one molecule of the substance is heavier than $\frac{1}{12}$ of the weight of one atom of carbon. Hence molecular weight of a substance

$$=\frac{\text{Weight of one molecule of the substance}}{\text{Weight of one atom of carbon}/12}$$

or, Molecular weight of a substance

$$=\frac{\text{Weight of one molecule of the substance}}{\text{Weight of one atom of carbon}}\times 12.$$

On this scale, the molecular weight of nitrogen is 28. This means that one molecule of nitrogen is 28 times heavier than $\frac{1}{12}$ of the weight of one atom of carbon. The molecular weight of a substance does not represent the true weight of the molecule of the substance. It gives the relative weight of the molecule. Hence it has no unit.

Gram-molecular weight or Gram-mole. A gram-molecular weight is defined as the weight in gram numerically equal to the molecular weight, i.e., the molecular weight expressed in gram is the gram-molecular weight. One gram-molecular weight of a substance is also known as one gram-mole or simply one mole. When it is known that the formula written for a substance is its correct molecular formula, the molecular weight and formula weight are of course the same and the mole equals the gram-formula weight. Again, as in gram-atomic weight, $6{\cdot}023\times10^{23}$ molecules are present in a mole of a substance. The molecular weight of water, H_2O is 18·016 and hence one mole of water is 18·016 grams in which $6{\cdot}023\times10^{23}$ molecules of water are present. Thus the formula for water, H_2O, represents not only the compound, water but also 18·0160 grams of water and $6{\cdot}023\times10^{23}$ molecules of water. Similarly, the formula $C_{12}H_{22}O_{11}$ represents $(12\times12+22\times1+11\times16)$ $=342$ grams or one gram-mole of sucrose or 1 mole of sucrose containing $6{\cdot}023\times10^{23}$ molecules of this compound.

It is now obvious that from the gram-molecular weight, we can easily calculate the absolute weight of the molecule.

Thus, absolute weight of the molecule $=\frac{\text{Gram-molecular weight}}{6{\cdot}023\times10^{23}}$

Thus, weight of one molecule of water $=\frac{18{\cdot}016}{6{\cdot}023\times10^{23}}$

$=2{\cdot}991\times10^{-23}$ gram.

It has been mentioned previously that the chemical formula allows us to determine the composition of a substance. The composition can be determined in terms of weight percentage of its component elements. The procedure can be lucidly demonstrated with the help of an example :

One molecule of sulphuric acid is represented by the formula H_2SO_4 which contains two atoms of hydrogen, one atom of sulphur and four atoms of oxygen. If one looks at the atomic weight table, one can at once know that

atomic weight of hydrogen = 1·008
atomic weight of sulphur = 32·066
atomic weight of oxygen = 16·000

Hence, the molecular weight of sulphuric acid can be calculated as

relative weights of 2 hydrogen atoms = 2 × 1·008 = 2·016
relative weights of 1 sulphur atom = 1 × 32·066 = 32·066
relative weights of 4 oxygen atoms = 4 × 16 = 64·000

Hence, the molecular weight of sulphuric acid = 98·082

Therefore, the percentage by weight of hydrogen $= \frac{2{\cdot}016}{98{\cdot}082} \times 100$

$= 2{\cdot}06$

the percentage by weight of sulphur $= \frac{32{\cdot}066}{98{\cdot}082} \times 100 = 32{\cdot}7$

and the percentage by weight of oxygen $= \frac{64{\cdot}00}{98{\cdot}082} \times 100 = 65{\cdot}2$.

Thus, we can determine the percentage by weight of any given element in the compound by the general formula :

percentage by weight of the element

$$= \frac{\text{relative weights of the element}}{\text{molecular weight of the compound}} \times 100.$$

In conclusion, we can note that each molecular formula represents the following :

(i) A shorthand method of writing the name of the substance.
(ii) One molecule of the substance.
(iii) One gram-molecular weight or one mole of the substance.

Number of molecules present in a gram-mole. Oxygen molecule is diatomic. Hence in one molecule of oxygen there are two oxygen atoms. Therefore, the molecular weight of oxygen is 32. Let us suppose that the molecular weight of an element = M.

The weight of a molecule of the element = m gram and the weight of an atom of oxygen = n gram. Hence on the oxygen scale, the molecular weight of the element

$$=\frac{\text{Weight of one molecule of the element}}{\text{Weight of one atom of oxygen/16}}$$

$$\therefore \quad M=\frac{m}{n}\times 16$$

We know that one gram-atomic weight of oxygen = 16 gram.

Weight of an atom of oxygen = n gram.

Therefore, the number of oxygen atoms present in one gram-atom of oxygen $=\frac{16}{n}$.

The number of molecules present in one gram-mole of the element $=\frac{M}{m}$.

$$\text{Now,} \quad M=\frac{m}{n}\times 16$$

$$\therefore \quad \frac{M}{m}=\frac{16}{n}. \quad \text{or,} \quad \frac{16}{n}=\frac{M}{m}.$$

Hence the number of atoms present in one gram-atom of oxygen is equal to the number of molecules present in one gram-mole of any substance. Therefore, one gram-mole of any substance contains the same number of molecules. By experiment it has been found that this number is $6{\cdot}023\times 10^{23}$ and is called the *Avogadro number*.

The number of gram-moles or moles (n) present in g gram of a substance of molecular weight M is given by

$$n=\frac{g}{M}.$$

or, the number of gram-moles or moles

$$=\frac{\text{Weight of the substance in grams}}{\text{Molecular weight of the substance}}.$$

2.13. Valency. In the study of the chemical compounds, one has known that atoms of different elements combine to form molecules of the compounds. The combining ability of different atoms is not the same. Thus some atoms appear to be able to attach to only 1 other atom, whereas other atoms can combine with 2 or 3 or 4. Let us consider the following compounds :

(i) Hydrogen chloride, HCl
(ii) Water, H_2O
(iii) Ammonia, NH_3
(iv) Methane, CH_4.

From these formulas, it appears that chlorine is capable of combining with one atom of hydrogen, whereas oxygen atom is capable of holding on two hydrogen atoms. Similarly, the nitrogen atom has the ability of combining with three hydrogen atoms whereas carbon atom is capable of combining with four hydrogen atoms. In no case the hydrogen atom is found to be combined with four carbon atoms, or three nitrogen atoms or in fact to more than one of any kind of atoms. Conseqently, an atom of hydrogen has the least combining capacity. This ability to combine with other elements is called the valency. The valency of an element is equal to the number of hydrogen atoms with which one atom of that element combines. Upon the simplest assumption that hydrogen has a valency of one, chlorine has also the valency of one because in the compound HCl, one atom of chlorine combines with one atom of hydrogen. Oxygen, then, has the valency of two, because one atom of oxygen combines with two atoms of hydrogen. Similarly, nitrogen has the valency of 3 and carbon has the valency of 4.

The valency of an element can be regarded as a number which represents the combining capacity of one atom of that element and is measured by the number of hydrogen atoms with which one atom of that element would combine.

An element with valency 1 is said to be univalent. The adjectives, bivalent, trivalent, quadrivalent or tetravalent, quinquevalent or pentavalent, hexavalent or sexivalent, heptavalent or septivalent and octavalent are used to describe elements with valences 2, 3, 4, 5, 6, 7 and 8 respectively.

If the element is not combined with hydrogen, usually its valency can be calculated from the valency of the other elements. For example, for $CaCl_2$, the valency of chlorine is known to be 1 in HCl.

Hence, the valency of calcium is 2 because one atom of calcium combines with two atoms of chlorine. In Fe_2O_3, two iron atoms combine with three oxygen atoms. Total valency of oxygen is $3\times2=6$. Since the total valency of oxygen must be equal to the total valency of iron, the total valency of iron in Fe_2O_3 must be equal to 6. Hence in Fe_2O_3, each iron atom has the valency of $\frac{6}{2}=3$.

An element shows its valency when it combines with other elements. In uncombined state, the element has the valency of zero.

The inert gases like helium, neon, argon, krypton, xenon, etc., cannot form any compound with other elements, i.e., they have no combining capacity. Hence the valency of the inert elements is always zero. Thus, there are, in all, nine valencies which are displayed by various elements, viz., 0, 1, 2, 3, 4, 5, 6, 7, and 8.

Variable valency. Under different conditions, some elements exhibit more than one valency. An element may exhibit more than one valency, either (i) in its compounds with the same elements or (ii) in its compounds with different elements. In the following illustrations, the above statement will be clear.

(i) Iron is bivalent in $FeCl_2$ and trivalent in $FeCl_3$.
Iron is bivalent in FeO and trivalent in Fe_2O_3.

(ii) Phosphorus is trivalent in phosphorus trichloride, PCl_3 and pentavalent in phosphorus pentachloride, PCl_5; nitrogen is trivalent in ammonia, NH_3 and pentavalent in nitrogen pentoxide, N_2O_5.

When a metallic element has more than one valency, modern nomenclature indicates the valency by writing a roman numerical in the parenthesis after the name of the element. Thus, $FeCl_3$ is written as iron (III) chloride and Fe_2O_3 as iron (III) oxide. $FeCl_2$ is written as iron (II) chloride and FeO is written as iron (II) oxide. In an older nomenclature, the higher valency is indicated, in the name, by the suffix "ic", whereas the lower valency is shown with the suffix "ous". Thus, $FeCl_3$ is ferric chloride and $FeCl_2$ is ferrous chloride. Fe_2O_3 is ferric oxide and FeO is ferrous oxide. Similarly, CuCl is cuprous chloride and $CuCl_2$ is cupric chloride. Hg_2Cl_2 is mercurous chloride and $HgCl_2$ is mercuric chloride.

If an element possesses variable velency and unites with both hydrogen and oxvgen, then it will exert its minimum valency in its hydrogen-compound and maximum valency in its oxygen-compound and the sum of the minimum valency and maximum valency is generally 8. This rule is known as *Abegg-Bodlander rule.* The rule is illustrated in the following table :

Compound	Valency of the element	Minimum valency +maximum valency
HCl Cl_2O_7	1 7	1+7=8
PH_3 P_2O_5	3 5	3+5=8
H_2S SO_3	2 6	2+6=8
CH_4 CO_2	4 4	4+4=8
NH_3 N_2O_5	3 5	3+5=8

2·14. **Radicals.** In many molecules, a group of atoms of different elements occurs more or less as a unit and behaves collectively like a single atom. For example, a simple group (OH) composed of one oxygen atom and one hydrogen atom occurs in many different compounds with many other elements. Such a group of atoms is called a radical. The OH group just mentioned is called the hydroxyl radical. *Radicals behave as units during a chemical reaction.* In ammonium chloride, NH_4Cl, the group of atoms, NH_4 behaves as a unit and plays the part of a univalent element. It is called the ammonium radical.

Let us consider sulphuric acid, H_2SO_4 as another example. In this compound, four oxygen atoms and one sulphur atom form a group giving rise to the sulphate radical (SO_4). The sulphate radical combines with two hydrogen atoms and hence its valency is 2. Thus in nitric acid, HNO_3 the nitrate radical, NO_3 combines with one hydrogen atom and, therefore, the valency of the nitrate radical is 1. Similarly, the phosphate radical, PO_4 is trivalent in H_3PO_4. The hydroxyl radical, OH is monovalent in NaOH because the valency of sodium is 1.

All elements and radicals do not combine with each other. The valencies of common elements and radicals are listed in table 2.2(a) and 2.2(b). The elements and radicals have been arranged in Tables 2.2(a) and 2.2(b). The elements and radicals in one table can combine with elements and radicals in the other table but the elements within the same table do not generally combine with each other. The reasons for such behaviour of them will become apparent later.

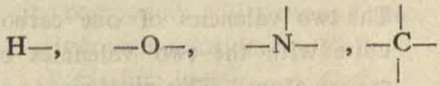
Table 2.2(a) : Common valencies of some elements and radicals.

Element	Radical	Symbol	Valency	Examples
	Ammonium	NH_4	1	NH_4Cl
Copper (I), Cuprous		Cu	1	CuCl
Copper (II), Cupric		Cu	2	$CuCl_2$
Hydrogen		H	1	HBr
Mercury (I), Mercurous		Hg	1	Hg_2Cl_2
Mercury (II), Mercuric		Hg	2	$HgCl_2$
Potassium		K	1	KCl
Silver		Ag	1	AgCl
Sodium		Na	1	NaCl
Barium		Ba	2	$BaCl_2$
Cadmium		Cd	2	$CdCl_2$
Calcium		Ca	2	$CaCl_2$
Cobalt (II), Cobaltous		Co	2	$CoCl_2$
Cobalt (III), Cobaltic		Co	3	$CoCl_3$
Iron (II), Ferrous		Fe	2	$FeCl_2$
Iron (III), Ferric		Fe	3	$FeCl_3$
Lead (II), Plumbous		Pb	2	$PbCl_2$
Lead (IV), Plumbic		Pb	4	$PbCl_4$
Magnesium		Mg	2	$MgCl_2$
Manganese (II), Manganous		Mn	2	$MnCl_2$
Manganese (IV), Manganic		Mn	4	$MnCl_4$
Nickel		Ni	2	$NiCl_2$
Strontium		Sr	2	$SrCl_2$
Tin (II), Stannous		Sn	2	$SnCl_2$
Tin (IV), Stannic		Sn	4	$SnCl_4$
Aluminium		Al	3	$AlCl_3$
Antimony		Sb	3	$SbCl_3$
Bismuth		Bi	3	$BiCl_3$
Chromium (II), Chromous		Cr	2	$CrCl_2$
Chromium (III), Chromic		Cr	3	$CrCl_3$
Carbon		C	4	CO_2
Silicon		Si	4	SiO_2

Table 2.2(b) : Common valencies of some elements and radicals.

Element	Radical	Symbol	Valency	Examples
	Acetate	(CH_3COO)	1	CH_3COOH
	Arsenite	(AsO_3)	3	K_3AsO_3
Bromine		Br	1	KBr
	Hydrogen carbonate	(HCO_3)	1	$NaHCO_3$
	Hypochlorite	(ClO)	1	$NaClO$
	Bisulphate	(HSO_4)	1	$NaHSO_4$
	Bromate	(BrO_3)	1	$NaBrO_3$
Chlorine		Cl	1	HCl
	Chlorite	(ClO_2)	1	$HClO_2$
	Chlorate	(ClO_3)	1	$KClO_3$
	Cyanide	(CN)	1	KCN
Fluorine		F	1	NaF
	Hydroxide	(OH)	1	$NaOH$
Iodine		I	1	NaI
	Nitrate	(NO_3)	1	$NaNO_3$
	Nitrite	(NO_2)	1	$NaNO_2$
	Perchlorate	(ClO_4)	1	$KClO_4$
	Permanganate	(MnO_4)	1	$KMnO_4$
	Carbonate	(CO_3)	2	K_2CO_3
	Chromate	(CrO_4)	2	K_2CrO_4
	Dichromate	(Cr_2O_7)	2	$K_2Cr_2O_7$
Oxygen		O	2	Na_2O
	Peroxide	(O_2)	2	Na_2O_2
	Sulphate	(SO_4)	2	H_2SO_4
	Sulphide	S	2	Na_2S
	Thiosulphate	(S_2O_3)	2	$Na_2S_2O_3$
	Manganate	(MnO_4)	2	K_2MnO_4
	Monohydrogen phosphate	(HPO_4)	2	K_2HPO_4
	Arsenate	(AsO_4)	3	Na_3AsO_4
	Borate	(BO_3)	3	Na_3BO_3
	Phosphate	(PO_4)	3	K_3PO_4
Phosphorus		P	3	PCl_3
			5	PCl_5

2.15. Structural formula. The valency of an element is often represented by the necessary number of hyphens drawn from the symbol of the element. Thus, the valency of hydrogen, oxygen, nitrogen and carbon can be pictorially represented as

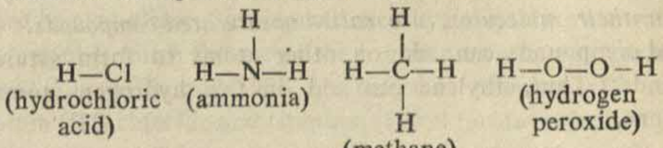


$$\mathrm{H}-,\quad -\mathrm{O}-,\quad -\overset{|}{\mathrm{N}}-\ ,\ -\underset{|}{\overset{|}{\mathrm{C}}}-$$

The number of hyphens corresponds to the valencies of the element. When atoms combine together, the hyphen on the symbol of one atom is joined with the hyphen on the symbol of the other atom. Thus, the combination of hydrogen and oxygen to form water can be pictorially represented as

$$\mathrm{H}\underset{\frown}{-\ \ -}\mathrm{O}\underset{\frown}{-\ \ -}\mathrm{H} \quad \rightarrow \quad \mathrm{H-O-H}$$

Each of the two hydrogen atoms is attached to the oxygen atom by a valence bond or linkage represented by the line connecting the symbols for the atoms. The pictorial representation of the linking of the atoms of a molecule in a definite order is known as *structural formula.* Hydrochloric acid, ammonia, methane and hydrogen peroxide can be represented by the structural formulas as



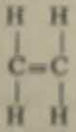
$$\mathrm{H-Cl} \qquad \mathrm{H}-\overset{\overset{\mathrm{H}}{|}}{\mathrm{N}}-\mathrm{H} \qquad \mathrm{H}-\underset{\underset{\mathrm{H}}{|}}{\overset{\overset{\mathrm{H}}{|}}{\mathrm{C}}}-\mathrm{H} \qquad \mathrm{H-O-O-H}$$

(hydrochloric acid) (ammonia) (methane) (hydrogen peroxide)

2.16. Saturated and Unsaturated compounds. In methane, CH_4, we see that 4 valencies of carbon are equal to the total valencies of hydrogen atoms. Similarly, in water, H_2O, two valencies of oxygen are equal to the total valencies of hydrogen atoms. In Al_2O_3, the total valencies of aluminium is equal to the total valencies of oxygen. The valencies of the elements in these compounds are said to be balanced. The compounds in which the valencies of the combining elements are balanced are called *saturated compounds.* Other examples of saturated compounds are ethane, propane, etc.

In some compounds such as C_2H_4, C_2H_2, etc., the valencies of the combining elements are not balanced. Thus, in C_2H_4, the total valencies of carbon is $2\times4=8$, and the total valencies of hydrogen is $4\times1=4$. In these compounds, two or more valencies of an atom of an element can unite with the corresponding number of valencies of an atom of the same element :

Ethylene,



$$\begin{array}{ccc} H & & H \\ | & & | \\ C & = & C \\ | & & | \\ H & & H \end{array}$$

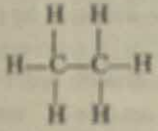
The two valencies of one carbon atom unite with the two valencies of other carbon atom. This gives rise to a double bond between carbon atoms.

Acetylene, $H-C\equiv C-H$

The three valencies of one carbon atom unite with the three valencies of the other carbon atom. This gives rise to a triple bond between carbon atoms.

When one valency of one carbon atom unites with one valency of the other carbon atom, we get a single bond between the carbon atoms :

Ethane,



$$\begin{array}{ccccc} & H & & H & \\ & | & & | & \\ H- & C & - & C & -H \\ & | & & | & \\ & H & & H & \end{array}$$

Compounds which have double or triple bonds between some of the atoms in their molecules, are called unsaturated compounds. Unsaturated compounds can add on other atoms to form saturated compounds. Thus, ethylene can add on two hydrogen atoms to give ethane.

2.17. The naming of compounds. An element can combine with some other elements to form different compounds. For example, two compounds of lead and chlorine are $PbCl_2$ and $PbCl_4$. This brings to light a problem of chemical nomenclature, i.e., naming of chemical compounds.

Compounds of two elements are called binary compounds. The names of the binary compounds are constructed from the names of the two elements in the particular compound. The name of the more metallic element is used as the first part of the name of the compound. The second part of the name of the compound consists of the stem of the name of the less metallic element together with the suffix "-ide." Thus, BaO is called barium oxide which is constructed as barium+(oxygen-ygen+ide)=barium oxide.

The name of $AlCl_3$ is constructed as

aluminium + (chlorine − ine + ide) = aluminium chloride. The name of Na_2S is sodium sulphide, i.e.,

sodium + (sulphur − ur + ide) = sodium sulphide. The names of the following compounds will serve as further illustrations :

HCl	Hydrogen chloride.	$NaBr$	Sodium bromide
KI	Potassium iodide.	CaC_2	Calcium carbide
Mg_3N_2	Magnesium nitride.	Cl_2O	Chlorine oxide
LiH	Lithium hydride.	NaF	Sodium fluoride.

For the case in which one element forms two or more compounds with some other elements, there are three schemes of nomenclature in common use. (i) The suitable prefixes are used to denote the number of atoms of a given kind. Thus, $PbCl_2$ is called lead dichloride and $PbCl_4$, lead tetrachloride. SO_2 and SO_3 are sulphur dioxide and sulphur trioxide respectively. (ii) The suffixes 'ous' and 'ic' are employed to denote the lower and higher valency of one of the elements in a binary compound. On this basis, $SnCl_2$ is called stannous chloride (stannum − um + ous) and $SnCl_4$, the stannic chloride (stannum − um + ic). (iii) When an element exhibits more than two valencies, the names of the compounds formed by that element are constructed by designating the valency of the element through the use of the roman numericals in parentheses. Thus, $TiCl_2$, $TiCl_3$ and $TiCl_4$ are named as titanium (II) chloride, titanium (III) chloride and titanium (IV) chloride respectively.

The names of some compounds illustrating the schemes are given below :

Cu_2O, cuprous oxide or copper (I) oxide ; CuO, cupric oxide or copper (II) oxide ; FeO, ferrous oxide or iron (II) oxide ; Fe_2O_3, ferric oxide or iron (III) oxide ; Hg_2Cl_2, mercurous chloride or mercury (I) chloride ; $HgCl_2$, mercuric chloride or mercury (II) chloride ; N_2O, nitrous oxide or nitrogen (I) oxide ; NO, nitric oxide or nitrogen (II) oxide.

In some oxides, the prefix 'per' is added to one containing most oxygen. Thus,

H_2O_2, hydrogen peroxide ; Na_2O_2, sodium peroxide.

The rules for naming somewhat more complicated molecules are discussed in a later chapter.

2.18. Derivation of formulas. The formula of many simple compounds may be written from the knowledge of the valencies of elements and radicals. A chemical compound is generally formed by the combination of an element with the element or radical having opposite valency. Thus, when an element X combines with another element or radical Y to form a compound, the valency of X must balance that of Y so that the valency of the compound as a whole is nil. Hence, the total valency of X must be equal and opposite to the total valency of Y. Thus, we can write

total valency of X = total valency of Y

i.e., number of atoms of X × valency of X = number of atoms of Y × valency of Y

$$\text{or,}\quad \frac{\text{number of atoms of X}}{\text{number of atoms of Y}} = \frac{\text{valency of Y}}{\text{valency of X}}$$

Therefore, we see that in a molecule of the compound of X and Y, the number of atoms of X and Y present is inversely as the valencies of X and Y.

To derive the formula of a molecule of a compound, the following procedure may be adopted.

(i) The symbols of the elements are written side by side. The more positive element is written at the left and the less positive element or radical is written at the right.

(ii) The valency of the left element is written at the bottom of the right element and the valency of the right element or radical is written at the bottom of the left element. When the valencies of the two elements are divisible by a common factor, they are first reduced to a simple ratio, and then the procedure is applied. The valency 1 is not generally written at the bottom. The examples in table 2.3 will clarify the above procedure. Consult the tables 2.2(a) and 2.2(b) for the valencies of the elements.

2.19. Chemical equation. In chapter I, it was pointed out that a chemical reaction is a process in which certain substances are converted into other substances. The substances which undergo chemical change are called reactants and those which are formed as a result of the chemical change are called products.

The chemist uses a system of "shorthand" writing to describe chemical reactions. This system employs symbols and formulas of substances instead of words. In a chemical equation, the formulas of the initial substances (the reactants) are always written to the left and the formulas of the products are written to the right of the equality sign. Thus, the reaction of sodium hydride and water can be represented as

Table 2.3

Compound	Symbols of		Valencies of		Formula
	left element	right element/ radical	left element	right element/ radical	
Sodium oxide	Na	O	1	2	Na_2O
Aluminium oxide	Al	O	3	2	Al_2O_3
Phosphorus pentachloride	P	Cl	5	1	PCl_5
Sulphuric acid	H	SO_4	1	2	$H_2(SO_4)$
Calcium phosphate	Ca	PO_4	2	3	$Ca_3(PO_4)_2$
Sodium bicarbonate	Na	HCO_3	1	1	$Na(HCO_3)$
Aluminium nitrate	Al	NO_3	3	1	$Al(NO_3)_3$
Aluminium phosphate	Al	PO_4	3	3	$Al_3(PO_4)_3$ or $AlPO_4$
Calcium oxide	Ca	O	2	2	CaO
Stannic oxide	Sn	O	4	2	SnO_2
Aluminium borate	Al	BO_3	3	3	$Al(BO_3)$

$$NaH + H_2O = H_2 + NaOH$$

The plus sign on the left side of the equality sign may be interpreted as "react with" and that on the right side may be interpreted as "and". The sign of equality is interpreted as "to form". Thus, the above equation tells us that sodium hydride "reacts with" water "to form" hydrogen "and" sodium hydroxide.

Balanced equation. A balanced equation is one which shows the same number of atoms of each element before and after the reaction. An unbalanced "equation" is really not an equation but a mere statement that a reaction occurs, it gives an incomplete picture of what is taking place.

Let us now consider the reaction between hydrogen and oxygen to form water :

$$\begin{array}{l} H_2+O_2=H_2O \\ \underbrace{2{\cdot}016\ \ 32}_{34{\cdot}016}\ \ 18{\cdot}016 \end{array}$$

Inspection of this "unbalanced equation" indicates several discrepancies. First, the equality is not realised since two atoms of oxygen are represented to the left of the sign of equality and only one atom on the right. Secondly, calculating the formula weights of each substance in the reaction from the atomic weights of H=1·008, O=16, we find that 34·016 parts by weight of the reactants are forming 18·016 parts by weight of products. It, therefore, seems that matter has been destroyed in this reaction which is contrary to the law of conservation of mass.

The above discrepancies can be removed by placing coefficients in front of the formulas, so that the numbers of each kind of atom on both sides of the above "equation" will be the same. Thus

$$2H_2+O_2=2H_2O$$

The placing of the coefficients before H_2 and H_2O is referred to as balancing the unbalanced equation. Note that the balanced equation shows that 36·032 parts of the reactants form 36·032 parts of the products.

Significance of a chemical equation. The chemical equation represents :

(i) A shorthand method of describing a chemical reaction.

(ii) The minimum number of particles taking part in the reaction—the unit reaction.

(iii) The weights, numbers of moles and volumes (in the case of gases) of substances involved in the chemical reaction.

Let us consider the following equation :

$$\begin{array}{ccccc} H_2 & + & Cl_2 & = & 2HCl \\ 2{\cdot}016 & & (2\times 35{\cdot}457) & & (2\times 36{\cdot}465) \end{array}$$

This equation tells us that (i) hydrogen reacts with chlorine to form hydrogen chloride ; (ii) one molecule of hydrogen and one molecule of chlorine take part in the reaction forming two molecules of hydrogen chloride.

(iii) 2·016 parts by weight of hydrogen react with 70·914 parts by weight of chlorine to form 72·93 parts by weight of hydrogen chloride. Since hydrogen, chlorine and hydrogen chloride are gases, we can also say "one volume of hydrogen combines with one volume of chlorine to form two volumes of hydrogen chloride."

Limitations of a chemical equation. A chemical equation cannot provide us informations on the following :

(a) Energy changes, i.e., whether heat is evolved or absorbed during the chemical reaction.

(b) Conditions such as temperature, pressure and other factors under which the reaction takes place.

(c) The rate at which the reaction proceeds and the time taken for its completion.

(d) The concentrations of the reacting substances and those of products formed.

(e) The physical states of the substances involved in the reaction.

Balancing chemical equations. During balancing a chemical equation, one must remember the following points :

(i) A chemical equation always represents a chemical reaction that really takes place in nature.

(ii) In a balanced equation, the numbers of each kind of atom on both sides of the equation will be the same.

(iii) The equation must represent the nature of the substance as they truly exist. Thus, oxygen exists as diatomic molecule, O_2 and, accordingly, oxygen should be written as O_2 in the equation. Iron does exist as individual atoms and hence iron is written in the equation as Fe.

2.20. Methods of balancing. All methods of balancing the chemical equation are based on the fact that the number of each species of atom on both sides of the balanced equation must be equal. Some systematic methods exist, some of which are discussed below :

Method 1. From the valencies of the reacting elements. This method is very useful for balancing the equations for simple reactions. Let us consider the following examples :

(i) Hydrogen reacts with oxygen to form water.

(a) Write the symbols and molecular formulas of the elements and compounds respectively in a skeleton equation. Thus

$$H+O=H_2O$$

(b) Place the valency of oxygen before hydrogen and that of hydrogen before oxygen. Thus

$$2H+1\cdot O=H_2O$$

(c) Represent hydrogen and oxygen as they truly exist, i.e., as H_2 and O_2. Hence

$$2H_2+1\cdot O_2=H_2O$$

(d) Finally, place the coefficient before H_2O such that the number of hydrogen and oxygen atoms on both sides of the equation become equal.

$$2H_2+O_2=2H_2O$$

This is a balanced equation. The numerical 1 is not generally placed before the molecule. The coefficient 2 in the term $2H_2$ means that two molecules of hydrogen, i.e., four hydrogen atoms altogether are involved in the reaction. The coefficient 2 in the term $2H_2O$ multiplies the entire formula H_2O, that is, $2H_2O$ means two molecules of H_2O (four hydrogen atoms and two oxygen atoms). Carefully study how the method has been applied on the following illustrations.

(1) Aluminium + Oxygen = Aluminium oxide
(a) $Al + O = Al_2O_3$
(b) $2Al + 3O = Al_2O_3$
(c) $4Al + 3O_2 = 2Al_2O_3$

Equation (c) is a balanced equation.

(2) Magnesium + nitrogen = Magnesium nitride
(a) $Mg + N = Mg_3N_2$
(b) $3Mg + 2N = Mg_3N_2$
(c) $3Mg + N_2 = Mg_3N_2$

Equation (c) is a balanced equation.

(3) Magnesium + Oxygen = Magnesium oxide
(a) $Mg + O = MgO$

(b) $2Mg + 2O = 2MgO$

(c) $2Mg + O_2 = 2MgO$

Equation (c) is a balanced equation.

(4) Aluminium + Sulphuric acid = Aluminium sulphate + Hydrogen

(a) $Al + H_2SO_4 = Al_2(SO_4)_3 + H_2$

(b) Since aluminium combines with SO_4, place the valency of aluminium before H_2SO_4 and that of sulphate before Al.

$$2Al + 3H_2SO_4 = Al_2(SO_4)_3 + 3H_2$$

This is a balanced equation.

(5) Sodium chloride+Sulphuric acid=Sodium sulphate +hydrochloric acid

(a) $NaCl + H_2SO_4 = Na_2SO_4 + HCl.$

(b) Place the valency of SO_4 before NaCl and that of sodium before H_2SO_4. The balanced equation is then obtained.

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl.$$

Method 2 : Balancing the equation representing a reaction in which there are one reactant and more than one products.

(1) **The decomposition of potassium chlorate :**

(i) Potassium chlorate=potassium chloride+oxygen

$$KClO_3 = KCl+O_2$$

(ii) There are 3 oxygen atoms on the left and 2 oxygen atoms on the right. Hence, we multiply the O_2 by $\frac{3}{2}$

$$KClO_3=KCl+\tfrac{3}{2}O_2$$

(iii) To eliminate the fraction we multiply the whole equation by 2

$$2KClO_3=2KCl+3O_2$$

(2) **Decomposition of hydrogen peroxide.**

Hydrogen peroxide=water+oxygen

(i) $H_2O_2 = H_2O+O$

(ii) $2H_2O_2 = 2H_2O+2O$

(iii) $2H_2O_2 = 2H_2O+O_2$

Equation (iii) is, evidently, a balanced equation.

Method 3 : Algebraic method for balancing equations :

This method is based upon the fact that the numbers of atoms of each element on both sides of the balanced equation must be equal. The reaction between potassium dichromate and hydrochloric acid can be taken as an illustration.

$$aK_2Cr_2O_7+bHCl=cKCl+dCrCl_3+eCl_2+fH_2O$$

This is an unbalanced equation. The coefficients a to f have been inserted before each molecular formula. The values of these coefficients can be calculated as follows :

Since the number of potassium (K) atoms on each side of the equation must be equal, we get

$$2a=c$$

From the similar consideration, we get

for the Cr atoms ; $2a=d$
for the O atoms ; $7a=f$
for the H atoms ; $b=2f$
for the Cl atoms ; $b=c+3d+2e$

The value '1' is then assigned arbitrarily to any of these coefficients. If a is put equal to 1, then we obtain

$c=2$; $d=2$; $f=7$; $b=14$ & $e=3$

The balanced equation, therefore, is

$$K_2Cr_2O_7+14HCl=2KCl+2CrCl_3+3Cl_2+7H_2O$$

Method 4 : Balancing by partial equations : This method involves writing intermediate equations. The intermediate equations are then added to get the final equation. The intermediate equations must be balanced by methods (1 – 3). The method is described completely in the following illustrations :

(i) Hydrogen peroxide reacts with an acid solution of potassium permanganate. The products are potassium sulphate, manganous sulphate, water and ogygen :

$$2KMnO_4=K_2O+2MnO+5O$$
$$K_2O+H_2SO_4=K_2SO_4+H_2O$$
$$2MnO+2H_2SO_4=2MnSO_4+2H_2O$$
$$5H_2O_2=5H_2O+5O$$
$$5O+5O=5O_2$$

$$2KMnO_4+3H_2SO_4+5H_2O_2=K_2SO_4+8H_2O+2MnSO_4+5O_2$$

(ii) Manganese dioxide reacts with hydrochloric acid to give manganese dichloride, water and chlorine.

$$\begin{array}{l} MnO_2+4HCl=MnCl_4+2H_2O \\ \quad MnCl_4=MnCl_2+Cl_2 \\ \hline MnO_2+4HCl=MnCl_2+2H_2O+Cl_2 \end{array}$$

(iii) Manganese dioxide + sodium chloride + sulphuric acid = Manganous sulphate + sodium bisulphate + chlorine + water.

i.e., $MnO_2+NaCl+H_2SO_4 \rightarrow MnSO_4+NaHSO_4+Cl_2+H_2O$

This reaction can be balanced as follows :

$$\begin{array}{l} 2NaCl+2H_2SO_4=2NaHSO_4+2HCl \\ MnO_2+H_2SO_4=MnSO_4+H_2O+O \\ 2HCl+O=H_2O+Cl_2 \\ \hline 2NaCl+MnO_2+3H_2SO_4=2NaHSO_4+MnSO_4+2H_2O+Cl_2 \end{array}$$

(iv) Ozone + hydrochloric acid = Chlorine + oxygen + water

$$O_3+HCl \rightarrow Cl_2+O_2+H_2O$$

The equation representing this reaction may be built up as

$$\begin{array}{l} O_3=O_2+O \\ 2HCl+O=H_2O+Cl_2 \\ \hline 2HCl+O_3=H_2O+Cl_2+O_2 \end{array}$$

(v) Chlorine reacts with a cold solution of sodium hydroxide to give sodium chloride, sodium hypochlorite and water. The equation for this reaction can be deduced as :

$$\begin{array}{l} Cl_2+H_2O=HCl+HOCl \\ HCl+NaOH=NaCl+H_2O \\ HOCl+NaOH=NaOCl+H_2O \\ \hline Cl_2+2NaOH=NaCl+NaOCl+H_2O \end{array}$$

2.21. **Types of chemical reactions.** Chemical reactions follow a number of patterns, some of which will be discussed.

1. **Combination or Synthesis.** [Synthesis (Syn—with ; tithemi —I place) means putting together]. When two or more substances (either element or compound) unite to form a single more complex substance, the chemical reaction is called combination or synthesis.

$$A+B \rightarrow C$$

When magnesium ribbon burns in air, the metal directly unites with oxygen of the air to form magnesium oxide.

$$2Mg+O_2=2MgO$$

When an electric spark is passed through a mixture of hydrogen and oxygen, hydrogen directly unites with oxygen to form water.

$$2H_2+O_2=2H_2O$$

Carbon dioxide combines directly with heated quicklime forming calcium carbonate.

$$CaO+CO_2=CaCO_3$$

These are few examples of combination reactions.

2. **Decomposition or Analysis.** When a compound breaks down into two or more simpler substances, the chemical reaction is called decomposition. It is exactly the reverse of combination.

$$C \rightarrow A+B$$

When strongly heated, red oxide of mercury breaks up into mercury and oxygen : $2HgO=2Hg+O_2$

We say that the mercuric oxide decomposes into mercury and oxygen.

When electric current is passed through acidulated water, water decomposes into hydrogen and oxygen.

$$2H_2O=2H_2+O_2$$

The breakdown of sugar by heat is another example of decomposition reaction :

$$C_{12}H_{22}O_{11}=12C+11H_2O$$

3. **Displacement or replacement.** It is a chemical reaction in which a more active element replaces another element in a compound and takes its place :

$$A+BC=B+AC$$

When zinc is added to sulphuric acid, it displaces hydrogen from sulphuric acid and forms zinc sulphate.

$$Zn+H_2SO_4=H_2+ZnSO_4$$

When a clean piece of iron is dipped into copper sulphate solution, iron goes into the solution to displace the copper, and red metallic copper is deposited.

$$Fe+CuSO_4=Cu+FeSO_4$$

4. **Double decomposition or metathesis.** The chemical reaction in which two compounds react by exchange of parts to form two new compounds, is called double decomposition or metathesis :

$$AB+CD=AD+CB$$

When a solution of sodium chloride is treated with a solution of silver nitrate, we get, by mutual exchange, sodium nitrate and silver chloride :

$$NaCl+AgNO_3=NaNO_3+AgCl$$

If a solution of potassium iodide is treated with a solution of mercuric chloride, double decomposition reaction takes place, and we get potassium chloride and mercuric iodide.

$$2KI+HgCl_2=2KCl+HgI_2$$

5. **Hydrolysis.** The chemical reaction in which a chemical compound reacts with water to form new substances is called hydrolysis.

Thus, phosphorus pentachloride reacts with water to give phosphoric acid and hydrochloric acid.

$$PCl_5+4H_2O=H_3PO_4+5HCl$$

Potassium cyanide when treated with water undergoes hydrolysis :

$$KCN+H_2O=KOH+HCN$$

When silicon tetrachloride is brought in contact with moist air, it hydrolyses, forming hydrochloric acid and orthosilicic acid :

$$SiCl_4+4H_2O=4HCl+H_4SiO_4 \text{ (orthosilicic acid)}$$

6. **Precipitation.** It is a process in which an insoluble solid separates by double decomposition when solutions of two substances are mixed together.

When a solution of barium chloride is mixed with a solution of potassium sulphate, a heavy white precipitate of barium sulphate is formed.

$$BaCl_2+K_2SO_4=BaSO_4+2KCl$$

When sulphuretted hydrogen gas is passed through a solution of copper sulphate, a black precipitate of copper sulphide is produced.

$$CuSO_4+H_2S=CuS+H_2SO_4$$

A yellow precipitate of lead chromate is formed when potassium chromate solution is mixed with the solution of lead acetate.

$$Pb(OOC.CH_3)_2+K_2CrO_4=PbCrO_4+2CH_3COOK$$

7. **Thermal dissociation.** Thermal dissociation is a phenomenon in which a molecule splits up into simpler parts on heating, but the latter recombine to form the original molecule on cooling.

The molecule which exhibits the phenomenon of dissociation is said to dissociate. Most of the ammonium salts dissociate on heating. Thus, when ammonium chloride is heated, it dissociates into ammonia and hydrochloric acid, but on cooling ammonia and hydrochloric acid recombine to give ammonium chloride.

The process is reversible and is represented as

$$NH_4Cl \rightleftharpoons NH_3 + HCl$$

Calcium carbonate, on heating, dissociates into calcium oxide and carbon dioxide ; the process is represented as

$$CaCO_3 \rightleftharpoons CaO + CO_2$$

Similarly, phosphorus pentachloride dissociates into phosphorus trichloride and chlorine :

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

Certain elements also dissociate on heating. Thus, iodine, on being heated, dissociates as follows :

$$I_2 \rightleftharpoons I + I$$

Sulphur, selenium, phosphorus, arsenic, etc., also dissociate when heated strongly.

There is another type of dissociation known as electrolytic dissociation which has been discussed later.

8. **Isomerism.** The existence of two or more substances having the same molecular formula but possessing different properties because of different molecular structures, is called isomerism ; the different substances are said to be isomers of each other.

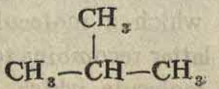
Ammonium cyanate, when heated, changes into urea by the simple rearrangement of atoms.

$$\underset{\text{(Ammonium cyanate)}}{NH_4(CNO)} \quad = \quad \underset{\text{(urea)}}{CO(NH_2)_2}$$

Ammonium cyanate and urea are said to be isomers. Similarly, two compounds are known that have the formula, C_4H_{10}. One of the compounds boils at -0.6°C and the other at -10°C, indicating that two different compounds having the same formula exist. These two compounds are normal butane and isobutane and hence they are isomers. The difference in the structural formula is shown for the two isomers :

$$CH_3{-}CH_2{-}CH_2{-}CH_3,$$

n-butane



$$CH_3{-}\overset{\overset{\displaystyle CH_3}{|}}{C}H{-}CH_3$$

iso-butane

When an isomeric change is reversible, it is called a tautomeric change.

9. **Polymerisation.** The reaction in which two or more molecules of a substance unite to form a molecule of another substance is called polymerisation.

$$\underset{\text{acetylene}}{3C_2H_2} \longrightarrow \underset{\text{benzene}}{C_6H_6}$$

2.22. **The phenomenon of allotropy.** *Allotropy is the property of an element by which it can exist in two or more forms which differ more or less in physical properties and in some chemical properties.*

The different forms of the element which exhibit allotropy are known as *allotropes.*

Ozone is a blue gas and has a fishy smell. It is a stronger oxidising agent than ordinary oxygen.

Although the properties of ozone are different from those of ordinary oxygen, it is not a compound but elementary oxygen in different form. In a molecule of oxygen (O_2), there are two atoms whereas in a molecule of ozone there are three oxygen atoms (O_3). Hence, ozone is an allotrope of oxygen.

Phosphorus exists in two allotropic modifications, e g., white phosphorus and red phosphorus. The properties of these two allotropes of phosphorus are quite different. White phosphorus melts at 44·1°C and red phosphorus at 590°C at 43 atmospheres. White phosphorus is extremely poisonous, but the red form is non-poisonous.

Allotropy is exhibited by numerous elements of which arsenic, antimony, bismuth, carbon, nitrogen, tin, iron, sulphur, etc., are few examples. It is due to the existence of two or more kinds of molecules (containing different number of atoms) or to the existence of two or more different crystalline forms.

The allotropes of some elements are mutually interconvertible and are described as enantiotropic (Greek—opposite, turning or change). For enantiotropic elements, there is a definite temperature called *the transition temperature* at which one form is transformed into the other. The interconversion of two crystalline varieties of sulphur takes place at 95·5°C which is the transition temperature of sulphur. When only one form is stable at all temperatures, the element is said to be monotropic.

Each allotrope of a given element is associated with a particular quantity of energy (internal energy). When one allotrope changes to another, a definite quantity of energy is either evolved or absorbed. This quantity of energy is equal to the difference between the quantities associated with each allotrope. 34,000 calories of heat are evolved when one mole of ozone decomposes to oxygen. When white phosphorus is converted into red phosphorus at temperatures above 250°C, so much heat is liberated that the reaction may become explosive.

Polymorphism. A compound may be able to form crystals of more than one variety. Compounds capable of such behaviour are called polymorphic and the phenomenon is called polymorphism. The term, polymorphism, is applied in the case of compound and the word, allotropy, is applied to the elements, be it solid, liquid or gaseous.

Isomorphism. Many substances have crystals of the same form. When two or more substances have the same crystalline form, the substances are called isomorphous and the phenomenon is known as isomorphism.

2.23. The phenomenon of catalysis. Frequently, the addition of an 'apparently inert' substance has the effect of increasing and sometimes of decreasing the rate of a chemical reaction. This substance remains unchanged in mass and in chemical composition at the end of the chemical reaction. The substance is called a catalyst, and is said to catalyse the reaction.

In order to get an insight of the phenomenon, let us consider an experiment : If we heat white crystals of pure potassium chlorate to a temperature of 368°C, the crystals melt to form a pale yellow liquid. At 368°C, however, the liquid potassium chlorate decomposes very slowly into potassium chloride and oxygen.

$$2KClO_3=2KCl+3O_2$$

But if we heat potassium chlorate to which a very small quantity of manganese dioxide has been added, we find that at 368°C potassium chlorate decomposes very rapidly. We also find that manganese dioxide remains unchanged in mass and in chemical composition after the reaction. Thus, our observations are that at 368°C.

(i) $KClO_3$ alone decomposes slowly.

(ii) $KClO_3$, in presence of MnO_2, decomposes very rapidly.

The inescapable conclusion from these observations is that the rate at which $KClO_3$ decomposes at 368°C is remarkably influenced by the mere presence of a foreign substance (e.g , MnO_2). Foreign substance may be recovered unchanged after the decomposition is complete. The influence of manganese dioxide upon the decomposition of potassium chlorate is an example of catalytic action or catalysis. Manganese dioxide is called a catalyst and the decomposition of $KClO_3$ is said to be catalysed by manganese dioxide.

Catalysis is a phenomenon in which the rate of a chemical reaction is increased or decreased by the addition of a small quantity of a foreign substance which remains unchanged in mass and in chemical composition at the end of the reaction.

The foreign substance is called a catalyst or catalytic agent.

Catalysts. *A catalyst is defined as a substance which has the property of either increasing or decreasing the rate of a chemical reaction, but does not itself undergo any change in mass and in chemical composition at the end of the reaction.*

The action of catalysts is highly selective. A substance that catalyses one reaction, may be wholly without influence towards another reaction, or a catalyst which increases the rate of one reaction, may decrease the rate of another reaction. Catalysts are extremely useful for promoting reactions which occur too slowly at ordinary temperatures, or whose products would be damaged if excessively high temperatures were used. In most cases, only a very small quantity of catalysts is required.

For the convenience of study, catalytic reactions are divided into two groups, e.g., heterogeneous and homogeneous catalysis :

(i) **Heterogeneous catalysis.** In the heterogeneous catalytic reactions, the catalyst is not uniformly distributed throughout the bulk of the reaction-mixture but forms a separate phase. Many examples of this type of catalysis are found in the use of solid catalysts to catalyse the reactions between gases. A mixture of hydrogen and oxygen may be kept at room temperature without reaction but if platinum is introduced into the mixture, combination of hydrogen and oxygen takes place on the surface of the metal, and water is formed. In this reaction, the platinum metal forms a separate phase (i.e., solid) from the reaction-mixture (gas). Other examples of heterogeneous catalysis are :

(i) finely divided platinum or vanadium pentoxide in the oxidation of sulphur dioxide to sulphur trioxide

$$(2SO_2+O_2=2SO_3).$$

(ii) reduced iron in the synthesis of ammonia from nitrogen and hydrogen $(N_2+3H_2=2NH_3)$

(iii) metallic copper in the reaction of ammonia and oxygen which takes place at 500°C, to yield nitrogen and steam

$$(4NH_3+3O_2=2N_2+6H_2O).$$

The phenomenon of catalysis in which a solid catalyst is used to catalyse a gaseous reaction is often styled as *contact catalysis*.

(ii) **Homogeneous catalysis.** In homogeneous catalysis, the catalyst is uniformly distributed throughout the bulk of the reaction-mixture, and all the substances are present in one single phase. Examples of this type of catalysis are :

(a) action of nitric oxide vapour in the oxidation of sulphur dioxide to sulphur trioxide

$$(2SO_2+O_2=2SO_3)$$

(b) the influence of acids in promoting the hydrolysis of cane sugar

$$(C_{12}H_{22}O_{11}+H_2O=C_6H_{12}O_6+C_6H_{12}O_6)$$

(c) the action of water in assisting the union of hydrogen chloride and ammonia to yield ammonium chloride

$$(HCl+NH_3=NH_4Cl)$$

Types of catalysis

(i) **Positive catalysis.** *A catalyst which increases the rate of a chemical reaction is called a positive catalyst, and the phenomenon is called positive catalysis.* Manganese dioxide acts as a positive catalyst in the decomposition of potassium chlorate into potassium chloride and oxygen. The platinum gauze in the oxidation of ammonia into nitric oxide

$$4NH_3+5O_2=6H_2O+4NO$$

acts as a positive catalyst.

In the commercial production of ammonia from nitrogen and hydrogen

$$N_2+3H_2\rightleftharpoons 2NH_3$$

metals such as platinum act as positive catalysts.

(ii) **Negative catalysis.** *The substance which decreases the rate of a chemical reaction is called a negative catalyst. The phenomenon is known as negative catalysis.* The negative catalyst is also called a *retarder* or an *inhibitor.*

The rate of decomposition of hydrogen peroxide into water and oxygen is decreased by the presence of small amount of phosphoric acid. In this reaction, phosphoric acid acts as a negative catalyst, and the process of decreasing the decomposition is known as negative catalysis. Glycerine acts as a negative catalyst in the oxidation of sodium sulphite (Na_2SO_3) to sodium sulphate (Na_2SO_4) by air. Alcohol retards the oxidation of chloroform ($CHCl_3$) to phosgene gas ($COCl_2$).

(iii) **Autocatalysis.** Often a reaction is catalysed by one of its products. For example, the reaction of potassium permanganate and oxalic acid in acid solution is catalysed by manganous sulphate, $MnSO_4$, which is formed as a result of the following reaction :

$$2KMnO_4+5H_2C_2O_4+3H_2SO_4=K_2SO_4+2MnSO_4+10CO_2+8H_2O$$

The rate of the reaction at first is very small but increases as the reaction progresses because manganous sulphate formed catalyses the reaction. *The phenomenon in which a reaction is catalysed by one of its products is called autocatalysis.*

The hydrolysis of ethyl acetate by water is autocatalytic.

$$CH_3COOC_2H_5+H_2O=CH_3COOH+C_2H_5OH$$

The acetic acid (CH_3COOH) which is produced as a result of the hydrolysis catalyses the reaction.

(iv) **Induced catalysis.** If air is passed through the solution of sodium arsenite, it is not oxidised into sodium arsenate by the oxygen of the air, but the solution of sodium sulphite is oxidised into sodium sulphate under the same condition. If air is passed through a mixture of sodium arsenite and sodium sulphite solution, both salts are simultaneously oxidised, although arsenite is not oxidisable individually by any of the substances present in the mixture. These types of reaction are called *induced catalytic reactions* and the phenomenon is known as *induced catalysis*.

$$Na_2SO_3 + Na_3AsO_3 + O_2 = Na_2SO_4 + Na_3AsO_4$$

Criteria of catalysis. The most important criteria of catalytic reactions are as follows :

(i) *A very small quantity of the catalyst is capable to effect an appreciable change in the rate of a chemical reaction.* Thus, when 1.7×10^{-4} gm. of colloidal platinum is added to 1 litre of hydrogen peroxide, the rate of decomposition of hydrogen peroxide is markedly increased. Another striking example to the point is the catalytic action of copper sulphate in the oxidation of sodium sulphite by air. The rate of this oxidation reaction is appreciably increased by the presence of copper sulphate at a concentration of only 10^{-13} gram-molecules per litre.

(2) *The catalyst remains unchanged in mass and in chemical composition at the end of the reaction.*

There is no permanent change in the chemical composition of the catalyst. The physical state of the catalyst may, however, be changed. Thus, when coarse lumps of manganese dioxide are used to catalyse the decomposition of potassium chlorate, the pieces are found to be disintegrated to a very fine powder at the end of the reaction. Bright metallic platinum when used to catalyse the combination of hydrogen and oxygen, becomes coated with finely divided black powder. This finely divided platinum is a much stronger catalytic agent than the polished metal.

(3) *A catalyst cannot start a chemical reaction but can only alter its speed.* Ostwald believed that the catalyst can only accelerate a reaction which is actually in progress. Thus, he supposed that the interaction of hydrogen and oxygen actually proceeds at room temperature but so slowly that it is beyond detection. The introduction of platinum black merely increases the speed of this pre-existing reaction.

According to other views, catalysts really initiate certain reactions. Thus, the combination of ammonia with hydrogen chloride, and the union of nitric oxide with oxygen do not take place in the absence of moisture. It is not, however, possible to say definitely whether these reactions are really initiated by moisture, even though a trace of it may have a very pronounced catalytic effect.

4. *A catalyst cannot alter the position of equilibrium in a balancd action ; the forward and backward reaction is accelerated to the same extent.* An example to the point is provided by the reaction of alcohol and acetic acid to form ethyl acetate and water,

$$C_2H_5OH + CH_3COOH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

The forward reaction is accelerated by acids, as also is the backward reaction, i.e., the hydrolysis of ethyl acetate by water. But the forward and the backward reactions are influenced by the acids to an equal extent so that final position of equilibrium remains unchanged.

Catalyst poisons. The presence of small quantities of certain substances, sometimes, causes a heterogeneous catalyst to lose its activity. *The substances which retard the chemical change by destroying the efficiency of an essential catalyst are known as anti-catalyst or catalyst poison.* The catalyst which is thus made ineffective is said to be poisoned. The catalyst poisons usually operate by reacting with the surface particles of the catalyst to change their composition or to 'coat' them.

The most well known example of catalyst poison is arsenious oxide. This catalyst poison destroys the catalytic activity of platinum which is used in the oxidation of sulphur dioxide to sulphur trioxide. So a special care is taken to remove this substance from sulphur dioxide in the manufacture of sulphuric acid by contact process. H_2S, HCN, $HgCl_2$, CO, etc., also act as catalyst poisons.

Catalyst promoters. Sometimes, a mixture of a catalyst and one or more foreign substances produces a greater catalytic effect than the catalyst alone. The foreign substances may not themselves be catalytically active. *The substances which increase the activity of the catalysts are called promoters.* For example, reduced iron acts as a catalyst in the synthesis of ammonia, but its catalytic activity is greatly increased when it is mixed with molybdenum or with a mixture of aluminium oxide and potassium oxide. Molybdenum or a mixture of aluminium oxide and potassium oxide acts as promoter.

Problems

1. How many gram-molecules or moles are present in 5 grams of water ? How many molecules of water are present in it ?

(a) The molecular formula of water is H_2O.

$\therefore$ Its molecular weight$=2\times1+16=18$

18 grams of water$=1$ gram-molecule of water

$\therefore$ 5 grams of water$=\frac{5}{18}=0{\cdot}277$ gram-mole of water.

$\therefore$ 0·277 gram-mole or 0·277 moles of water are present in 5 grams of water.

(b) 18 grams of water contain $6{\cdot}023 \times 10^{23}$ molecules of water.

∴ 5 grams of water contain $\frac{6{\cdot}023 \times 10^{23} \times 5}{18} = 1{\cdot}668 \times 10^{23}$ molecules of water.

∴ $1{\cdot}668 \times 10^{23}$ molecules of water are present in 5 grams of water.

2. *Calculate the amount of ammonia in grams present in 0·17 gram-mole of ammonia.*

Molecular formula of amonia is NH_3.

∴ Molecular weight of ammonia $= 14 + 1 \times 3 = 17$

∴ 1 gram-mole of ammonia $= 17$ grams.

∴ $0{\cdot}17$ gram-mole of ammonia $= 17 \times {\cdot}17 = 2{\cdot}89$ grams.

∴ 2·89 grams of ammonia are present in 0·17 gram-mole of ammonia.

3. *How many oxygen atoms are present in 0·9 gram of water ?*
[*H. S., '78*]

Molecular formula of water is H_2O.

∴ Its molecular weight $= 1 \times 2 + 16 \times 1 = 18$

18 grams of water contain $6{\cdot}023 \times 10^{23}$ molecules of water.

∴ 0·9 gram of water contain $\frac{6{\cdot}023 \times 10^{23} \times 0{\cdot}9}{18} = 30{\cdot}08 \times 10^{21}$ molecules of water.

Now, 1 molecule of water contains 1 oxygen atom

∴ 0·9 gram of water contain $30{\cdot}08 \times 10^{21}$ atoms of oxygen.

4. *Calculate the number of molecules present in the solution obtained by dissolving 10·26 grams of cane sugar in 36 grams of water.* $C = 12$, $O = 16$, $H = 1$.

Molecular formula of cane sugar is $C_{12}H_{22}O_{11}$.

Molecular weight of water $= 18$

Molecular weight of cane sugar

$$= 12 \times 12 + 22 \times 1 + 11 \times 16 = 342$$

18 grams of water contain $6{\cdot}023 \times 10^{23}$ molecules of water

∴ 36 grams of water contain $\frac{6{\cdot}023 \times 10^{23} \times 36}{18} = 12{\cdot}046 \times 10^{23}$ molecules of water.

342 grams of sugar contain $6{\cdot}023 \times 10^{23}$ molecules of sugar.

∴ 10·26 grams of sugar contain $\frac{6.023\times10^{23}\times10.26}{342}$

$=0.18069\times10^{23}$ molecules of sugar.

∴ Total number of molecules

$=12.046\times10^{23}+0.18069\times10^{23}=12.22669\times10^{23}$.

5. *What is the weight of 10 molecules of oxygen ?*

1 oxygen molecule contains 2 atoms of oxygen

∴ Molecular weight of oxygen $=16\times2=32$

Now, 6.023×10^{23} molecules of oxygen weigh 32 grams.

∴ 10 molecules of oxygen weigh

$$\frac{32\times10}{6.023\times10^{23}}=53.1\times10^{-23}\text{ gram.}$$

6. *Calculate the number of molecules of water present in 1·8 c.c. of water at 4°C.* [*H. S., '84*]

The density of water at 4°C = 1

∴ Mass of 1·8 c.c. of water = 1·8 gram.

Molecular weight of water = 18

∴ 18 grams of water contain 6.023×10^{23} molecules of water.

∴ 1·8 gram of water contain

$$\frac{6.023\times10^{23}\times1.8}{18}=6.023\times10^{22}\text{ molecules of water.}$$

7. *How many oxygen atoms are present in 0·4 mole of carbon dioxide ? And how many moles of oxygen atom are present in it ?*

(a) The molecular formula of carbon dioxide is CO_2.

1 mole of carbon dioxide contains 6.023×10^{23} molecules of carbon dioxide.

∴ 0·4 mole of carbon dioxide contains $6.023\times10^{23}\times0.4$

or, 2.4092×10^{23} molecules of carbon dioxide.

Now, 1 molecule of carbon dioxide contains 2 atoms of oxygen.

∴ 2.4092×10^{23} molecules of carbon dioxide contain

$2.4092\times10^{23}\times2$. or 4.8184×10^{23} atoms of oxygen.

(b) 6.023×10^{23} atoms of oxygen ≡ 1 mole of oxygen atoms.

∴ 4.8184×10^{23} atoms of oxygen

$$\equiv\frac{4.8184\times10^{23}}{6.023\times10^{23}}\equiv0.8\text{ moles of oxygen atoms.}$$

∴ 0·4 mole of carbon dioxide contains 0·8 moles of oxygen atoms.

8. *How many grams of hydrogen are needed to react completely with 128 grams of oxygen ?*

Hydrogen reacts with oxygen according to the following equation :

$$\begin{array}{cccccc} 2H_2 & + & O_2 & = & 2H_2O \\ 2\times 2 \text{ gram} & & 32 \text{ gram} & & 2\times 18 \text{ gram} \end{array}$$

$\therefore$ 32 grams of oxygen react with 4 grams of hydrogen.

$\therefore$ 128 grams of oxygen react with

$$\frac{4\times 128}{32}=16 \text{ grams of hydrogen.}$$

Hence 16 grams of hydrogen are needed to react completely with 128 grams of oxygen.

9. *How many moles of hydrogen will be required in order to react completely with 1597 grams of Fe_2O_3 ?*

(Mol. wt. of $Fe_2O_3=159{\cdot}7$)

$$3H_2 + Fe_2O_3 = 3H_2O + 2Fe$$

$\therefore$ 3 moles of hydrogen react with 1 mole of Fe_2O_3.

Now, 159·7 grams of $Fe_2O_3 \equiv 1$ mole of Fe_2O

$\therefore$ 1597 grams of $Fe_2O_3 \equiv 10$ moles of Fe_2O_3.

Now, 1 mole of Fe_2O_3 reacts with 3 moles of hydrogen.

$\therefore$ 10 moles of Fe_2O_3 react with 30 moles of hydrogen.

$\therefore$ 1597 grams of Fe_2O_3 react with 30 moles of hydrogen.

EXERCISE

I

1. Define the terms—(a) atom, (b) molecule, (c) atomic weight, and (d) molecular weight.

What do you understand by the absolute weight of an atom and a molecule ?

2. Distinguish between element and compound giving examples of each.

3. Which of the materials listed below are (a) elements, (b) compounds, or, (c) mixtures ?

(i) Milk, (ii) Calcium, (iii) Iron, (iv) Calcium carbonate, (v) Alum, (vi) Blood, (vii) Aluminium, (viii) Iodine, (ix) Table salt, (x) Sugar, (xi) Sand, (xii) Copper.

4. What are symbols and formulas ? What is the complete significance of the symbol 'O' ? With whom did modern symbols have their origin ? What is the significance of the formula, H_2O ? What informations can be deduced from this formula ?

Is it correct to write the formula $H_{1 \cdot 6}O_{0 \cdot 8}$? If not why ?

5. What do you understand by valency of elements ? How is it measured ?

6. "The valency of an element can vary". Explain the statement clearly with examples.

7. What do you understand by "structural formula" ? What are "saturated" and "unsaturated" compounds ?

8. Write down the formula of the following compounds and calculate their moelcular weights.

(a) Sodium chloride
(b) Ammonium carbonate
(c) Calcium sulphate
(d) Phosphorus pentoxide
(e) Magnesium phosphate
(f) Tin (IV) chloride
(g) Stannic chromate
(h) Copper nitrate
(i) Potassium chlorite
(j) Barium permanganate
(k) Iron (II) sulphate
(l) Calcium hydride.

9. What is a chemical equation ? What informations are expressed in a chemical equation ? Why must chemical equations be balanced ? What are the limitations of a chemical equation ?

10 Write equations for the reactions that occur when

(a) Sulphur and oxygen combine to form a compound having formula, SO_3.

(b) Iron and chlorine combine to form the compound, $FeCl_3$.

(c) Sodium reacts with water to form hydrogen and the compound, NaOH.

(d) Phosphorus reacts with oxygen to form phosphorus pentoxide.

(e) The reactants are $CaBr_2$ and H_2SO_4, and the products are $CaSO_4$ and HBr.

(f) The two compounds $Ca(OH)_2$ and H_3PO_4 react to form water and $Ca_3(PO_4)_2$.

(g) The reactants are CH_4 and chlorine, and the products are chloroform ($CHCl_3$) and HCl.

(h) The reactants are N_2 and H_2, and the product is NH_3.

(i) Potassium chlorate ($KClO_3$) when heated gives potassium chloride and oxygen.

(j) The compound, Fe_2O_3, reacts with hydrogen to form iron and water.

11. Translate the following equations into symbols.

(i) Sodium hydroxide + sulphuric acid = Sodium sulphate + water.

(ii) Calcium carbonate (limestone) + hydrochloric acid = Calcium chloride + water + carbon dioxide

(iii) Zinc + sulphuric acid = Hydrogen + zinc sulphate.

(iv) Ferrous sulphide + sulphuric acid = Ferrous sulphate + sulphuretted hydrogen.

(v) Silver nitrate + potassium chloride = Silver chloride + potassium nitrate.

(vi) Barium chloride + sodium sulphate = Barium sulphate + sodium chloride.

(vii) Lead acetate + potassium chromate = Lead chromate + potassium acetate.

(viii) Copper sulphate + sulphuretted hydrogen = Copper sulphide + sulphuric acid.

(ix) Calcium oxide + water = Calcium hydroxide (slaked lime)

(x) Stannic chloride = Stannous chloride + chlorine.

(xi) Sodium carbonate + hydrochloric acid = Sodium chloride + water + carbon dioxide.

(xii) Ammonia + oxygen = Nitric oxide + water.

12. Balance the following equations :

(a) $NaOH + HCl \rightarrow NaCl + H_2O$

(b) $Fe_2O_3 + H_2 \rightarrow Fe + H_2O$

(c) $Na_2O_2 + H_2O \rightarrow NaOH + O_2$

13. Balance the following equations by algebraic method :

(i) $NaCl + H_2SO_4 + MnO_2 \rightarrow NaHSO_4 + MnSO_4 + H_2O + Cl_2$

(ii) $Pb_3O_4 + HCl \rightarrow PbCl_2 + H_2O + Cl_2$

(iii) $KMnO_4 + H_2SO_4 + H_2S \rightarrow K_2SO_4 + MnSO_4 + H_2O + S$

(iv) $I_2 + NaOH \rightarrow NaI + NaIO_3 + H_2O$

(v) $KMnO_4 + H_2SO_4 + H_2O_2 \rightarrow K_2SO_4 + MnSO_4 + H_2O + O_2$

(vi) $FeSO_4 + H_2SO_4 + H_2O_2 \rightarrow Fe_2(SO_4)_3 + H_2O$

(vii) $HI + H_2SO_4 \rightarrow I_2 + SO_2 + H_2O$

14. Prove the following :

(a) One gram-atom of all elements contain the same number of atoms.

(b) One gram-molecule or one mole of all substances contain the same number of molecules.

15. Write notes on (a) allotropy, (b) catalysis, (c) thermal dissociation and thermal decomposition.

II

1. How many gram-molecules and molecules are present in 10 grams of calcium carbonate ? [Ans. 0·1 gram-molecule ; $0{\cdot}6023 \times 10^{23}$]

2. How many oxygen atoms are present in 9·8 grams of sulphric acid ? [Ans. $2{\cdot}4092 \times 10^{23}$]

3. How many carbon atoms and moles of oxygen atoms are present in 1·76 grams of carbon dioxide ? [Ans. $2{\cdot}4092 \times 10^{22}$; 0·08 moles]

4. Has the molecule of chlorine greater weight than that of sodium ? If so why ? [Ans. Yes.]

5. Which one has greater number of molecules ?

(a) 20 grams of calcium carbonate and 20 grams of sulphuric acid. [Ans. Second compound]

(b) 2 grams of hydrogen and 20 grams of nitrogen. [Ans. First compound.]

(c) 10 grams of carbon dioxide, 10 grams of calcium carbonate and 10 grams of sulphuric acid. [Ans. First compound.]

(d) 6 grams of carbon dioxide, 6 grams of sulphur dioxide and 6 grams of nitrogen dioxide. [Ans. First compound.]

Explain your answer.

6. If water and acetone (C_3H_6O) are mixed in the ratio of 1 : 1 (by weight), then what will be the ratio of gram-moles in the mixture ? What will be the ratio of molecules in the mixture ? [Ans. 29 : 9]

7. 3·42 grams of sugar are dissolved in 1·8 grams of water. What is the number of oxygen atoms in the mixture ? [Ans. $1{\cdot}26483 \times 10^{23}$]

8. Oxygen and hydrogen are mixed in the ratio of 2 : 3 by weight.

(a) What is the ratio of molecules of the two gases in the mixture ?

(b) What is the number of hydrogen molecules in the mixture ?

[Ans. (a) 1 : 24 (b) $1{\cdot}8069 \times 10^{23}$]

9. 1 gram of naphthalene ($C_{10}H_{22}$) is dissolved in 10 grams of ethyl alcohol (C_2H_5OH).

(i) What is the number of molecules of naphthalene in 1 gram of the solution ?

(ii) What is the number of molecules of naphthalene in 1 gram of ethyl alcohol ? [Ans. (i) $3{\cdot}83 \times 10^{20}$ (ii) $4{\cdot}2161 \times 10^{20}$]

10. How many moles of hydrogen will react with 7·95 grams of cupric oxide ? Cu = 63·5 [Ans. 0·1 mole]

11. How many moles of carbon dioxide will be evolved when 10 grams of calcium carbonate are heated ? Ca = 40 [Ans. 0·1 mole]

CHAPTER III

THE LAWS OF CHEMICAL CHANGE AND THE ATOMIC THEORY

3.1. Introduction. To the alchemists, chemical reactions must have seemed mysterious beyond comprehension. Modern chemistry had its beginning with the development of quantitative technique by which meaningful experimental data concerning chemical reactions were first obtained. Out of such data have come most of the laws and theories of chemical science. The study of chemical reactions from the quantitative standpoint is called *stoichiometry*.

3.2. The laws of chemical combination by weight. There are five laws which describe how compounds are built up of elements :

(1) The law of conservation of mass.

(2) The law of definite proportions.

(3) The law of multiple proportions.

(4) The law of reciprocal proportions.

(5) The law of gaseous volumes.

Of these the first four laws are related to the weights of the combining elements and are known as laws of stoichiometry. The last law deals with the volumes of the combining gases.

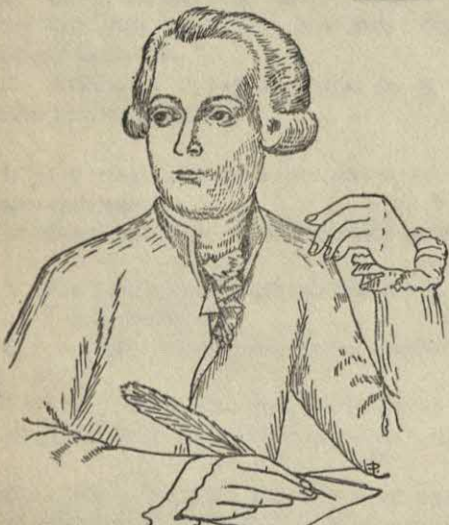


Fig. 3.1. Lavoisier (1743—1794).

(1) **Law of conservation of mass or the law of indestructibility of matter.** Till now, we have known that whenever a chemical

reaction occurs, the reactants disappear and new kinds of matter are formed. At the same time, energy, often in the form of heat, is either evolved by the reactants to the surroundings or absorbed from them.

Most fundamental of the laws governing the behaviour of mass or matter in a chemical reaction, is the *law of conservation of mass or matter.* It states that *mass can be neither created nor destroyed.* Whenever a chemical process is carried out, the total mass of the reactants is equal to the total mass of the products of reaction. Early scientific workers assumed the existence of this law. Lomonosov in 1756 and Lavoisier in 1774 verified the law experimentally. They calcined tin in a sealed flask and found that no change of weight took place.

Experimental verification of the law of conservation of mass. **Experiment 1.** A conical flask containing potassium chloride solution is taken. A test tube containing silver nitrate solution is next placed into the flask. The flask is then corked and weighed. The conical flask is then tilted when the following reaction occurs :

$$KCl + AgNO_3 = AgCl + KNO_3$$

When the reaction is complete, the flask is reweighed. No alteration in the weight is observed. This proves that the total mass of the reactants is equal to the total mass of the products.

Experiment 2. Landolt's experiment. Between 1893 and 1908, Landolt carried out a series of experiments with the object of testing the truth of the law. He chose fifteen reactions in which the evolution or absorption of heat is negligibly small, one of these reactions is taken as an example :

Solutions of hydriodic acid and of iodic acid are mixed to yield water and a precipitate of iodine.

$$5HI + HIO_3 = 3I_2 + 3H_2O$$

The experimental arrangement of Landolt is shown in fig. 3.2. The solution of hydriodic acid is placed in one limb of the H-tube and the solution of iodic acid in the other limb. The H-tube is then sealed. The tube is then accurately weighed by means of a balance sensitive to 1 part in 10,000,000. It is then removed from the balance and inverted so that the solutions can mix well with each other and the reaction takes place. The tube is then allowed to stand for a long time so that it may attain the temperature of the room. When the tube is again weighed by the balance, its weight is found to remain unchanged.

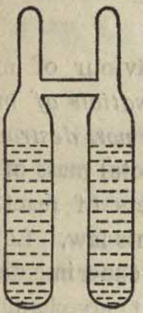


Fig. 3.2

Relation between the law of conservation of mass and the law of conservation of energy. These two laws together form the basis of all experimental investigations. It is now believed that mass and energy are interconvertible. The relation between mass and energy is given by an important equation known as the Einstein equation :

$$E = mc^2$$

In this equation, E is the energy corresponding to a mass, m, and c is the velocity of light. The velocity of light c is $2{\cdot}9979 \times 10^{10}$ cm./sec which is one of the fundamental constants of nature.

From the Einstein equation, it is evident that an evolution of energy in a chemical reaction should be accompanied by a loss of mass equal to E/c^2. *Mass is, therefore, no longer regarded as indestructible by a chemical change.* However, the mass lost by conversion to energy is so small in comparison with the quantities of matter taking part in chemical reactions that it is quite beyond detection by the most sensitive balance. For example, 1 calorie of heat* is equivalent to $4{\cdot}6 \times 10^{-14}$ gram. When 12 grams of carbon are converted to carbon dioxide 25,400 calories of heat are evolved. Hence, the decrease in mass will be $4{\cdot}6 \times 10^{-14} \times 25{,}400$ or $11{\cdot}684 \times 10^{-10}$ gram. Such a minute mass cannot be detected even by the most sensitive balance. Thus, the emission of energy in normal chemical reactions is accompanied by change in mass which is so minute that it is convenient to state the laws of mass and energy separately. But

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$$*m = \frac{E}{c^2} = \frac{1\ \text{cal}}{9 \times 10^{20}(\text{cm/sec})^2} = \frac{4{\cdot}2 \times 10^7\ \text{erg}}{9 \times 10^{20}(\text{cm/sec})^2}$$

$$= 4{\cdot}6 \times 10^{-14}\ \text{gram}$$

$$\therefore\ 1\ \text{calorie} = 4{\cdot}6 \times 10^{-14}\ \text{gram.}$$

when the absolute precision is required, the two laws are combined into a single law known as the law of conservation of Mass-Energy which may be stated as :

The sum of the quantity of matter and the energy in an isolated system is always constant.

(2) **The law of definite or constant proportions.** The law of constant or definite proportions was enunciated by the French Chemist, Joseph Louis Proust, in 1799. It states that : *Different samples of a given chemical compound always contain the same elements united in the same definite proportions by weight.*

Let us have different samples of the compound MN which contains the elements M and N. The different samples of the compound MN have been prepared in different ways. Then the law states that all the samples of the compound will contain the same elements M and N and no other elements. If in a sample of MN, m grams of M unite with n grams of N and in another sample of MN, x grams of M unite with y grams of N, then the law states that

$$\frac{m}{n}=\frac{x}{y}$$

Illustrations. (1) It was found by analysis that two elements, hydrogen and oxygen, are present in the compound, water, in the proportion by weight 1 : 8. One gram of hydrogen combines with 8 grams of oxygen to form 9 grams of water. Different samples of water can be obtained from different sources. Then the law of definite proportion states that *each and every sample of water collected from different sources contains the same elements, hydrogen and oxygen, united in the same ratio 1 : 8.*

(2) Sodium chloride can be prepared by different methods. It can be obtained from different sources, i.e., from sea water, from inside the mines, etc. Now, when all the samples of sodium chloride are analysed, it is invariably found that in every sample 23 grams of sodium are combined with 35·5 grams of chlorine to form 58·5 grams of sodium chloride. This proves that in all samples of sodium chloride, sodium and chlorine are present in the fixed definite ratio 23 : 35·5.

Experimental verification of the law of definite proportions. Let us take three different samples of cupric oxide and call them as sample no. 1, sample no. 2, and sample no. 3. These three samples of cupric oxide are prepared by three different methods.

Preparation of sample no. 1. Copper turnings are dissolved into 1 : 1 nitric acid. The solution thus formed is evaporated to dryness. The green copper nitrate which is formed is strongly heated when it decomposes to yield black cupric oxide.

Preparation of sample no. 2. To a solution of copper turnings in nitric acid, sodium carbonate solution is added in excess, when blue precipitates of copper carbonate are formed. The solution is filtered, and the precipitates are washed and dried. On being ignited, the precipitates give black cupric oxide.

Preparation of sample no. 3. To a solution of copper sulphate in water, sodium hydroxide is added in excess when pale blue precipitates of cupric hydroxide are formed. The solution is filtered and the precipitates are washed, dried and heated to give black cupric oxide.

Experiment with sample no. 1. A porcelain boat is cleaned and dried. It is then weighed by means of a sensitive balance. The process of cleaning and drying is repeated till a constant weight is obtained. Then a small amount of cupric oxide from sample no. 1 is taken into the boat and weighed again. A hard glass tube is clamped in a horizontal position as shown in fig. 3.3. The boat with cupric oxide is now introduced into the tube through which dry hydrogen gas is passed. The tube is heated strongly when cupric oxide is reduced to metallic copper. After

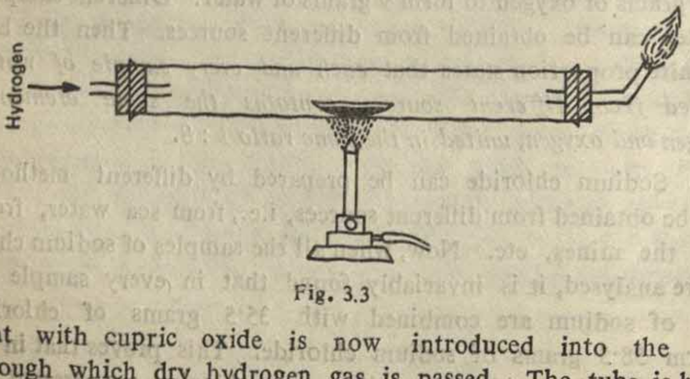

Fig. 3.3

the reaction is complete, the boat with reduced copper is cooled in a slow stream of hydrogen in the tube. It is taken out of the tube, kept for some time in a desiccator and weighed again. The boat is again introduced into the tube and heated again in a stream of hydrogen gas. The process is repeated until a constant weight of the boat is obtained. The data so obtained are represented as follows :

Weight of the empty boat $= W_1$ grams.
Weight of the boat + cupric oxide $= W_2$ grams.
Weight of the boat + copper $= W_3$ grams.
$\therefore$ Weight of cupric oxide $= (W_2 - W_1)$ grams.
Weight of copper $= (W_3 - W_1)$ grams.
$\therefore$ Weight of oxygen $= (W_2 - W_1) - (W_3 - W_1) = (W_2 - W_3)$ grams.

Hence, the percentage of copper in cupric oxide $= \dfrac{(W_3 - W_1)}{(W_2 - W_1)} \times 100$

The percentage of oxygen in cupric oxide $= \dfrac{(W_2 - W_3)}{(W_2 - W_1)} \times 100$

The actual experimental result is : % Cu = 79·89 ; % oxygen = 20·11. In other words, 100 grams of CuO contain 79·89 grams of copper and 20·11 grams of oxygen and hence 79·57 (i.e., 63·57 + 16) grams of cupric oxide contain 63·57 grams of copper and 16 grams of oxygen.

Hence, in sample no. 1, copper and oxygen are present in the proportions by weight 63·57 : 16.

The experiment is repeated with samples no. 2 and 3. It is found that copper and oxygen are present in all these different samples in the same proportion by weight, i.e., 63·57 : 16.

The converse of the law of definite proportions is not always true. That is, the same elements may combine in the same definite proportions by weight to give two or more different compounds. Hence, if it is found that two compounds have the same composition by weight, it does not necessarily follow that they are one and the same substance. This is due to the existence of the phenomenon of *isomerism*. These different compounds with the same composition are called isomers. Urea $CO(NH_2)_2$ and ammonium cyanate, NH_4CNO have the same chemical composition and the same molecular formula, N_2H_4CO, yet they are entirely different in their properties. Butyl alcohol, C_4H_9OH, and ethyl ether $(C_2H_5)_2O$ are further examples of isomers.

There are exceptions to the law of definite proportions. For example, the two isotopes of lead, viz., Pb-206 and Pb-208 are obtained from two different sources. Hence, if two samples of Pb(II) chloride are prepared from lead, obtained from these sources then their molecular weights will be $(206+2\times35{\cdot}5)=277$ and $(208+2\times35{\cdot}5)=279$ respectively. Therefore, the ratio by weight of lead and chlorine in the above samples of Pb(II) chloride will be different.

Hence, the law of definite proportions is applicable to the compounds of the elements whose atomic weights remain invariable from whatever sources they may be obtained.

2. **The law of multiple proportions.** The law of multiple proportions was formulated by John Dalton in 1803. It states that *when two elements combine to form two or more different compounds, the several weights of one element which combine with the same weight of another element are in the ratio of small integers.*

Illustrations. (i) The law may be illustrated by the two compounds of hydrogen and oxygen, viz., water and hydrogen peroxide. It is found by experiment that

(a) in water, 1·008 grams of hydrogen unite with 8 grams of oxygen to form 9·008 grams of water.

(b) in hydrogen peroxide, 2·016 grams of hydrogen combine with 32 grams of oxygen, i.e., 1·008 grams of hydrogen combine with 16 grams of oxygen to form 17·008 grams of H_2O_2.

Thus, in these compounds, the different weights of oxygen, viz., 8 grams and 16 grams combine with the same weight of hydrogen (viz., 1·008 grams). 8 grams and 16 grams are in the ratio of small integers 1 and 2 (i.e., 8 gram : 16 gram or 1 : 2).

(ii) There are five different compounds of nitrogen and oxygen. It is found by analysis that

(a) in introus oxide, N_2O

14 grams of nitrogen unite with 8 grams of oxygen to form 22 grams of nitrous oxide.

(b) in nitric oxide, NO
14 grams of nitrogen unite with 16 grams of oxygen to form 30 grams of nitric oxide.

(c) in nitrogen trioxide, N_2O_3
14 grams of nitrogen unite with 24 grams of oxygen to form 38 grams of nitrogen trioxide.

(d) in nitrogen tetroxide, N_2O_4
14 grams of nitrogen unite with 32 grams of oxygen to form 46 grams of nitrogen tetroxide.

(e) in nitrogen pentoxide, N_2O_5
14 grams of nitrogen combine with 40 grams of oxygen to form 54 grams of nitrogen pentoxide.

In all these compounds, the different weights of oxygen, viz., 8 grams, 16 grams, 24 grams, 32 grams and 40 grams combine with the same weight (viz., 14 grams) of nitrogen. Now 8, 16, 24, 32 and 40 are found to be in the ratio of small integers, i.e., 1 : 2 : 3 : 4 : 5.

(iii) The law can also be illustrated by the two compounds of carbon and oxygen. By analysis of these compounds, we find that

(a) in carbon monoxide, CO,
16 grams of oxygen combine with 12 grams of carbon to form 28 grams of carbon monoxide.

(b) in carbon dioxide, CO_2,
16 grams of oxygen unite with 6 grams of carbon to form 22 grams of carbon dioxide.

Thus, in these two compounds, the same weight of oxygen, viz., 16 grams combine with different weights of carbon, viz., 12 grams and 6 grams which are in simple ratio 2 : 1.

(iv) Iron unites with chlorine to form two different compounds, viz., ferrous chloride and ferric chloride. By analysis of these two compounds of iron, we find that

in ferrous chloride, $FeCl_2$,
71 grams of chlorine unite with 55 84 grams of iron to form 126·84 grams of ferrous chloride.

in ferric chloride, $FeCl_3$,
106·5 grams of chlorine unite with 55·84 grams of iron to form 162·34 grams of ferric chloride.

Thus, different weights of chlorine, viz., 71 grams and 106·5 grams unite with the same weight of iron. They are in the ratio 71 : 106·5 or 2 : 3.

(v) Finally, we shall illustrate the law with the four hydrides of carbon. We find by chemical analysis that

(a) in case of acetylene, C_2H_2 :
24 grams of carbon unite with 2 grams of hydrogen to form 26 grams of acetylene.

(b) in ethylene, C_2H_4,
24 grams of carbon unite with 4 grams of hydrogen to form 28 grams of ethylene.

(c) in ethane, C_2H_6 :
24 grams of carbon unite with 6 grams of hydrogen to form 30 grams of ethane.

(d) in methane, CH_4 :
12 grams of carbon unite with 4 grams of hydrogen to form 16 grams of methane, i.e., 24 grams of carbon unite with 8 grams of hydrogen to form 32 grams of methane.

Thus, in all these hydrides, the different weights of hydrogen, viz., 8 grams, 6 grams, 4 grams and 2 grams have united with the same weight of carbon, viz., 24 grams. They are in ratio 8 : 6 : 4 : 2 or 4 : 3 : 2 : 1.

Experimental verification of the law. Copper forms two well defined oxides called respectively the cuprous oxide (Cu_2O) and cupric oxide (CuO). These two oxides can be easily reduced to metallic copper by hydrogen. Hence, they are most suitable for the verification of the law. Two porcelain boats are taken and marked as boat no. 1 and boat no. 2. They are cleaned and dried and weighed till a constant weight is obtained.

Now, some amount of dry black cupric oxide are taken into the boat no. 1 and weighed. Then the boat is placed in a hard glass tube placed horizontally as shown in the figure 3.3. The oxide is heated in a stream of hydrogen gas when it loses its oxygen which combines with the hydrogen to form water.

$$CuO+H_2=Cu+H_2O$$

When the cupric oxide has been completely reduced, the Bunsen burners are removed and the reduced copper is allowed to cool in a stream of hydrogen. When quite cold, the boat and its content are weighed. The boat and its content are again placed in the tube and heated in a stream of hydrogen again. The process is repeated until a constant weight of the boat is obtained.

The same experiment is performed with boat no. 2 containing cuprous oxide. The experimental data are represented as follows :

Boat no. 1 containing CuO	Boat no. 2 containing cuprous oxide, Cu_2O
Let us suppose that	Let us suppose that
(i) weight of empty boat $=W_1$ grams.	(i) the weight of empty boat $=a$ grams.
(ii) weight of boat+cupric oxide $=W_2$ grams.	(ii) the weight of boat+cuprous oxide $=b$ grams.
(iii) weight of boat+metallic copper $=W_3$ grams.	(iii) the weight of boat+copper $=c$ grams.
∴ weight of copper $=(W_3-W_1)$ grams.	∴ weight of copper $=(c-a)$ grams.
∴ weight of oxygen $=(W_2-W_3)$ grams.	weight of oxygen $=(b-c)$ grams.
Hence, (W_3-W_1) grams of copper unite with (W_2-W_3) grams of oxygen. Therefore, 63·57 grams of copper combine with $\frac{W_2-W_3}{W_3-W_1}\times 63{\cdot}57$ grams $=x$ grams (say) of oxygen.	Hence, $(c-a)$ grams of copper combine with $(b-c)$ grams of oxygen. Therefore, 63·57 grams of copper unite with $\frac{(b-c)}{(c-a)}\times 63{\cdot}57$ $=y$ grams (say) of oxygen.

It is found by actual experiment that x grams and y grams of oxygen which have combined with the same weight of copper are in the ratio 2 : 1.

The discovery of isotopes has shown that the law of multiple proportions is not of absolutely universal application. For example, lead (II) chloride, $PbCl_2$ can be prepared from Pb-206 obtained from uranium mineral and lead (IV) chloride, $PbCl_4$ can be prepared from Pb-208 obtained from thorium mineral. In these two compounds, the different weights of lead (viz., 103 grams and 52 grams) which combine with the fixed weight of chlorine (35·5 grams) are in the ratio 103 : 52. This is not the ratio of simple integers. Hence the law of multiple proportions is not applicable to these compounds.

Therefore, the law of multiple proportions is applicable to compounds prepared from the same isotope of the element or from elements in which the proportions of their isotopes always remain fixed. Except a few elements, the proportion of the isotopes remain fixed in most elements. For this reason, the law of multiple proportions is found to be true in most cases.

3. The law of reciprocal proportions. This law was discovered by Richter in 1792. It states that *the proportions by weight in which two elements separately combine with another element are in a simple ratio to the proportions by weight in which the two elements combine with one another.*

Let the elements A and B combine with another element C to form the compounds AC and BC. Let us suppose that in AC, x grams of A combine with 'a' grams of C ; in BC, y grams of B combine with 'a' grams of C.

Then the proportion by weight in which A and B combine with the element C is $x : y$. The law states that the proportion by weight in which A and B combine with one another should be equal to $mx : ny$ where m and n are small whole numbers.

Illustrations. (a) Let us consider the three elements carbon, hydrogen and oxygen. Hydrogen and oxygen can unite with carbon to produce methane and carbon dioxide respectively. Again, they can combine among themselves to form water and hydrogen peroxide.

(i) In methane, CH_4, 12 grams of carbon are combined with 4 grams of hydrogen.

(ii) In carbon dioxide, CO_2, 12 grams of carbon are combined with 32 grams of oxygen.

Hence, the proportion by weight in which hydrogen and oxygen combine with carbon is 4 : 32 or 1 : 8. Now,

(i) In water H_2O ; 2 grams of hydrogen combine with 16 grams of oxygen.

(ii) In hydrogen peroxide, H_2O_2 ; 2 grams of hydrogen combine with 32 grams of oxygen.

In water, the proportions by weight in which hydrogen and oxygen combine is 2 : 16 or $2 \times 1 : 2 \times 8$, Hence, m=n=2

In hydrogen peroxide, the ratio is 2 : 32 or $2 \times 1 : 4 \times 8$.

Hence, m=2 and n=4.

(b) The law can be illustrated by the following three compounds.

(i) In carbon dioxide, CO_2, 12 grams of carbon combine with 32 grams of oxygen.

(ii) In sulphur dioxide, SO_2, 32 grams of sulphur combine with 32 grams of oxygen.

Hence, proportion by weight in which carbon and sulphur combine with oxygen is 12 : 32 or 3 : 8.

(iii) In carbon disulphide, CS_2, 12 grams of carbon combine with 64 grams of sulphur.

Hence, the proportion by weight in which carbon and sulphur combine with each other=12 : 64 or 3 : 16=$1 \times 3 : 2 \times 8$

Hence, m=1 and n=2.

The law of reciprocal proportion implies that *when elements are brought into combination, numbers known as equivalents can be assigned to the elements, such that the ratio of the weights in which elements react is equal to the ratio of their equivalents.* For this reason, the law is also known as the law of equivalent proportions or the law of combining weights.

3·3. Gay-Lussac's law of combining volumes. In 1805, Gay-Lussac carried out some experiments on reactions between gases from which he enunciated a law known as the law of combining volumes. The law may be stated as :

The volumes of gases (at the same temperature and pressure) that react with one another or are produced in a chemical reaction are in the ratio of small whole numbers.

Illustrations. (1) When 200 c.c. of hydrogen are mixed with a large volume of oxygen, these two gases react to form water, the volume of oxygen used up in the reaction is exactly 100 c.c. Although much more oxygen than this are present in the reaction system, only 100 c.c. are actually used to form 200 c.c. of gaseous water, i.e., steam. This experimental result is described by saying that two volumes of hydrogen [200 c.c.=(2×100)] react with one volume of oxygen to form two volumes of steam and their volumes are in the ratio 2 : 1 : 2.

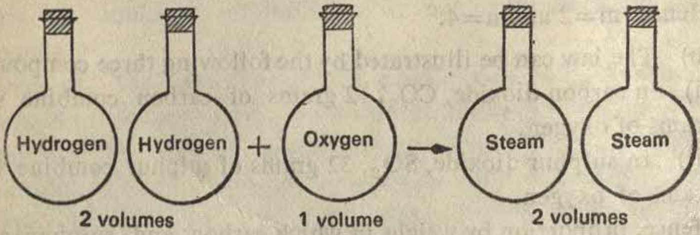

Fig. 3.4

(2) When the reaction between gases, hydrogen and chlorine, is studied, it is found that 1 litre of hydrogen is exactly enough to react completely with 1 litre of chlorine to produce 2 litres of the gas, hydrogen chloride. Or, 1 volume of hydrogen combines with 1 volume of chlorine to yield 2 volumes of hydrogen chloride and their volumes are in the ratio 1 : 1 : 2.

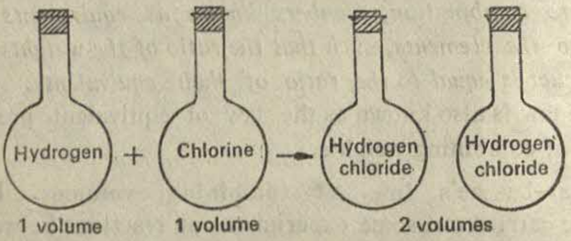

Fig. 3.5

(3) Similarly, it is found that one volume of nitrogen reacts with three volumes of hydrogen to yield 2 volumes of ammonia and their volumes are in the ratio 1 : 3 : 2.

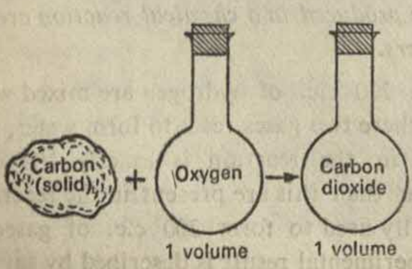

Fig. 3.6

(4) When the substances other than gases take part in the reaction, the same kind of volume relationship is found to exist. For example, 1 litre of oxygen reacts with solid carbon to yield 1 litre of carbon dioxide.

Or, one volume of oxygen reacts with solid carbon to yield one volume of carbon dioxide and the volume of oxygen and the volume of carbon dioxide are in the ratio of two small whole numbers, i.e., 1 : 1.

3.4. Dalton's Atomic Theory. The laws of conservation of mass, definite proportions, and reciprocal proportions were discovered* from the experimental facts concerning chemical change. There must exist some orderly state of affairs which gives rise to the simple laws noted. Thus, there is a need to formulate a theory which can explain all such laws.

Fig. 3.7 : John Dalton (1766—1844)

The man who proposed such a theory concerning the fundamental nature of chemical species was John Dalton, an English School Master. In 1808, in order to explain chemical behaviour, he made simple postulates which are now collectively known as Dalton's Atomic Theory. These are :

(i) Elements are composed ultimately of very minute, discrete particles called atoms. Atoms remain undivided in all chemical changes.

(ii) Each kind of atom has a definite weight.

(iii) Atoms of the same element are identical in all properties and equal in weight.

(iv) Atoms of the different elements have different properties and differ in weights.

(v) Compounds are formed by the union of integral numbers of atoms of different elements in simple numerical proportions as 1 : 1, 1 : 2, 2 : 3, 1 : 3, etc.

Thus, when the two elements A and B combine chemically to form a compound, it is the individual atoms of the element A and B that undergo change. The union of the atoms of A and B takes place in numerical ratios as follows :

---

*Note : The law of multiple proportions was not induced from experimental results, but was derived from the Dalton's atomic theory and was then tested by experiments.

(i) 1 atom of A unites with 1 atom of B. numerical ratio 1 : 1
(ii) 1 atom of A unites with 2 atoms of B. numerical ratio 1 : 2
(iii) 2 atoms of A unite with 1 atom of B. numerical ratio 2 : 1
(iv) 2 atoms of A unite with 3 atoms of B. numerical ratio 2 : 3, etc.

It will be interesting to examine the Dalton's postulates in the light of the modern theories regarding the structure of matter. It is seen in the light of the modern nuclear theory that the postulates are not rigorously true. But as far as fundamental viewpoint is concerned, Dalton's atomic theory is valid and sufficient for the calculations in chemical stoichiometry. He assumed that the atoms are indivisible but actually they can undergo decomposition. In natural radioactivity, the atoms of elements such as uranium and radium are undergoing decomposition into simpler atoms. In recent years, the splitting of the atoms of some of the elements into simpler atoms has been possible. Again, Dalton assumed that all atoms of the same element have the same weight but at present it has been found by sophisticated physical method that all atoms of the same element do not have the identical weights (isotopes). However, when a chemical change takes place, so many number of atoms are involved and mixed together that any collection of them will have statistically the same average atomic weight. It is this average atomic weight which is important in chemistry. Thus, although our knowledge about the structure of matter have become much more sophisticated, the basic truth of the Dalton's atomic theory remains untarnished. This can be realised when it is applied to explain the laws of chemical stoichiometry.

3.5. Explanation of the laws of chemical change. The laws of chemical combination by weights discussed in the preceding paragraph can be derived from the Dalton's atomic theory.

(1) **The law of conservation of mass.** According to Dalton, atoms are indivisible and cannot be created or destroyed. Hence, in a chemical reaction, though the atoms interchange partners, their nature and number before and after the reaction remain unchanged. As each atom has a definite mass, the total mass before and after the chemical reaction must be constant.

As a concrete example, let us consider the formation of water from the elements, hydrogen and oxygen. The atomic theory explains this reaction as the union of two atoms of hydrogen and one atom of oxygen to yield one molecule of water. One molecule of water also contains two atoms of hydrogen and one atom of oxygen. The total number of atoms before and after the reaction thus remains the same. Since the mass of each atom is invariant, mass of one molecule of water is equal to the sum of the masses of two atoms of hydrogen and one atom of oxygen.

(2) **The law of definite proportions.** According to the atomic theory, a compound is formed by the union of integral number of atoms in simple numerical proportions and each atom has a definite weight.

Let m atoms of the element A unite with n atoms of B to form the compound $A_m B_n$ where m and n are small whole numbers. Let each atom of element A has a definite weight x grams and each atom of B has a definite weight y grams. The ratio m : n must be constant for the compound $A_m B_n$ since by atomic theory atoms are not created or destroyed in forming a particular compound. Hence, in all samples of the compound $A_m B_n$ we must have,

$$\frac{\text{weight of A}}{\text{weight of B}}=\frac{\text{m} \times \text{weight of one atom of A}}{\text{n} \times \text{weight of one atom of B}}=\frac{\text{m} \times \text{x}}{\text{n} \times \text{y}}=\text{constant.}$$

This means that the compound $A_m B_n$ has a definite composition by weight. This is the law of definite proportions. Hence, the weights of m atoms of A, i.e., m × x grams and the weights of n atoms of B, i.e., n × y grams are constant for the particular compound, $A_m B_n$.

(3) **The law of multiple proportions.** Let us assume that the two elements A and B unite with each other to give two different compounds, viz., $A_m B_n$ and $A_s B_r$ where m, n, s and r represent the number of atoms. Let the weight of each atom of A is x grams and weight of each atom of B is y grams. By Dalton's atomic theory, the weights of each atom of A and B in $A_m B_n$ are the same as the weights of each atom of A and B in $A_s B_r$ and m, n, s, and r are small integers. Now, in $A_m B_n$, the weights of m atoms of A are m × x grams and the weights of n atoms of B are n × y grams. Hence, in $A_m B_n$, m × x grams of A combine with n × y grams of B.

$\therefore$ x grams of A combine with $\frac{n \times y}{m}$ grams of B.

Similarly,
In A_sB_r, $s \times x$ grams of A combine with $r \times y$ grams of B

$\therefore$ x grams of A combine with $\frac{r \times y}{s}$ grams of B.

The ratio of the different weights of B which combine with the same weight of A, i.e., x grams of A is

$$\frac{n \times y}{m} : \frac{r \times y}{s} = ns : mr$$

Since n and s are whole numbers their product ns will also be another whole number. Similarly, mr will be equal to a whole number. Hence, the weights of B which combine with the same weight of A are in the simple ratio. Thus, law of multiple proportions is derived from the atomic theory.

(4) **The law of reciprocal proportions.** Let us consider the three elements A, B and C. A separately combines with B and C to give two compounds, viz., A_mB_n and A_sC . Let the weight of each atom of A, B and C are x grams, y grams and z grams respectively. Let us assume that B and C combine together to produce the compound B_pC_q.

According to the atomic theory, the weight of each atom of A are the same in all compounds. Similar is the case with B and C. Again, m, n, s, r, p and q represent the number of atoms and are all whole numbers. Hence,

In A_mB_n, $m \times x$ grams of A unite with $n \times y$ grams of B

$\therefore$ x grams of A unite with $\frac{n \times y}{m}$ grams of B.

In A_sC_r, $s \times x$ grams. of A unite with $r \times z$ grams of C

$\therefore$ x grams of A unite with $\frac{r \times z}{s}$ grams of C.

Hence, the proportion by weight in which C and B combine with the element A is

$$\frac{n \times y}{m} : \frac{r \times z}{s} = \frac{(ns)}{(mr)} \times \frac{(y)}{(z)} \qquad (7{\cdot}2)$$

Now, in B_p C_q, $p \times y$ grams of B combine with $q \times z$ grams of C.

Hence, the proportion by weight in which B and C unite is

$$\frac{py}{qz} \tag{7·3}$$

Therefore, we get from (7·2) and (7·3)

$$\frac{\text{the proportion by weight in which B and C combine with the element A}}{\text{the proportion by weight in which B and C combine with one another}}=\frac{G}{H}$$

$$=\frac{ns}{mr}\times\frac{y}{z}\Big/\frac{py}{qz}=\frac{ns}{mr}\times\frac{y}{z}\times\frac{qz}{py}=\frac{nsq}{mrp}=\frac{(ns)}{(mr)}\times\frac{(q)}{(p)} \tag{7·4}$$

Since m, n, p, q, and r are all whole numbers, the numerator and denominator of (7·4) are in simple ratio. Thus, we find that the law of reciprocal proportions follows from the Dalton's atomic theory.

3.6. Usefulness of Dalton's atomic theory. (1) Dalton's atomic theory points out that atom is the smallest particle of matter. This idea, first of all, threw light on the structure of matter.

(2) From this theory, it is first known that in chemical reactions the atoms of different elements combine together in definite proportions to form compounds.

(3) The laws of chemical combinations except the law of gaseous volumes can be explained in the light of Dalton's atomic theory.

(4) "All atoms of the same elements have the same weights"—this idea was very helpful in the determination of atomic weights. On the basis of these atomic weights of the elements the periodic table was subsequently drawn up.

(5) Dalton's atomic theory played an extremely important role in the invention of Avogadro's hypothesis.

(6) "All atoms of the same element have the same weight and same properties"—this idea was very helpful in the introduction of the symbols and formulas. This idea also helped in expressing chemical reactions in the form of equations.

(7) "Atoms are indivisible smallest particles of matter which can take part in chemical reactions"—this idea of Dalton is the basic building stone of chemistry.

3.7. Drawback of Dalton's atomic theory. (1) Dalton called the smallest particles of both elements and compounds the atoms. But the smallest particles of compounds or molecules of compounds are formed by the combination of the atoms of the constituent elements. There is no mention of the concept of molecule in the Dalton's atomic theory.

(2) Gay-Lussac's law of combining volumes cannot be explained with the help of Dalton's atomic theory.

(3) After the discovery of isotopes, it has been found that the atoms of the same element may have different weights.

(4) In recent years, the splitting of the atoms of some of the elements into simpler atoms has been possible.

(5) In interstitial compounds and compelx polymers the atoms of the constituent elements are not present in the simple ratio of small whole numbers.

Problems

Ex. 1. *Zinc oxide was prepared by two different methods. In the first method 1·092 grams of zinc were converted into 1·352 grams of oxide by dissolving it into nitric acid and igniting the nitrate. In the second method 0·63 gram of the metal was converted into 0·78 gram of the oxide by dissolving the metal in hydrochloric acid precipitating as carbonate and igniting the carbonate. Show that these results illustrate the law of definite proportions.*

Method I. Weight of oxygen $= 1{\cdot}352 - 1{\cdot}092 = 0{\cdot}26$ gram.

Hence, $\dfrac{\text{Weight of zinc}}{\text{Weight of oxygen}} = \dfrac{1{\cdot}092}{0{\cdot}26} = 4{\cdot}2$

Method II. Weight of oxygen $= 0{\cdot}78 - 0{\cdot}63 = 0{\cdot}15$ gram.

Hence, $\dfrac{\text{Weight of zinc}}{\text{Weight of oxygen}} = \dfrac{0{\cdot}63}{0{\cdot}15} = 4{\cdot}2$

Thus, the ratio is constant for the two samples of zinc oxide. This proves the law of constant proportions.

Ex. 2. *A metal forms two oxides. On heating 1 gram of each oxide in a stream of hydrogen, 0·798 and 0·888 gram of the metal were obtained. Show how these results illustrate the law of multiple proportions.* [*Cal., '31*]

In the first oxide,

The weight of oxygen$=(1{\cdot}00-0{\cdot}798)=0{\cdot}202$ grams.

Hence, 0·798 gram of the metal unites with 0·202 gram of oxygen.

$\therefore$ 1 gram of the metal unites with $\dfrac{0{\cdot}202}{0{\cdot}798}=0{\cdot}2531$ gram of oxygen.

In the second oxide,

The weight of oxygen$=1{\cdot}000-0{\cdot}888=0{\cdot}112$ gram.

Hence, 0·888 gram of the metal unites with 0·112 gram of oxygen.

$\therefore$ 1 gram of the metal unites with $\dfrac{0{\cdot}112}{0{\cdot}888}=0{\cdot}1261$ gram of oxygen.

Hence, the weights of oxygen uniting with the same weight of the metal are 0·2531 gram and 0·1261 gram and their ratio is 0·2531 : 0·1261 or 2 : 1. Thus, the law of multiple proportions is illustrated.

Ex. 3. *Tin forms two oxides. In the oxide A, the per cent of tin by weight is 88·15 and in the oxide, B, the per cent of tin by weight is 78·81. Show that the results agree with the law of multiple proportions.*

In the oxide A, per cent of oxygen by weight$=100-88{\cdot}15=11{\cdot}85$

Hence, 88·15 grams of tin unite with 11·85 grams of oxygen.

$\therefore$ 1 gram of tin unites with $\dfrac{11{\cdot}85}{88{\cdot}15}$ gram of oxygen

$=0{\cdot}134$ gram of oxygen

In the oxide B, per cent of oxygen by weight$=100-78{\cdot}81=21{\cdot}19$

Hence, 78·81 grams of tin unite with 21·19 grams of oxygen

$\therefore$ 1 gram. of tin unites with $\dfrac{21{\cdot}19}{78{\cdot}81}=0{\cdot}268$ gram. of oxygen.

Therefore, the weights of oxygen which combine with a constant weight of tin, viz., 1 gram are as $0{\cdot}134 : 0{\cdot}268=1 : 2$. Thus, the data presented in the problem prove the law of multiple proportion.

Ex. 4. *A metal M forms two oxides. The oxide A contains 27·6% of oxygen and the oxide B contains 30·0% of oxygen. If the formula of A be M_3O_4, find that of B.* [*Cal.*, '40]

In the oxide A, the percentage of oxygen$=27{\cdot}6$

$\therefore$ the percentage of metal$=72{\cdot}4$

Hence, 100 grams of the oxide A contains 27·6 grams of oxygen and 72·4 grams of the metal M. Now, the formula of the oxide is M_3O_4. If the atomic weight of M is A, then

$$\frac{\text{Number of atoms of M}}{\text{Number of atoms of oxygen}}=\frac{3}{4}=\frac{72{\cdot}4/A}{27{\cdot}6/16}$$

(∵ 16 is the atomic weight of oxygen)

$$\therefore \quad A=\frac{72{\cdot}4\times16\times4}{27{\cdot}6\times3}=55{\cdot}936$$

In the oxide B, the percentage of oxygen = 30

∴ the percentage of the metal = 70·0

Hence, 100 grams of the oxide B contain 30 grams of oxygen and 70 grams of the metal M. Hence,

$$\frac{\text{Number of atoms of M}}{\text{Number of atoms of oxygen}}=\frac{70/55{\cdot}936}{30/16}=\frac{2}{3}$$

∴ Formula of the oxide B is M_2O_3.

Ex. 5. *Illustrate the law of reciprocal proportions from the following data :*

Sulphur hydride	*xygen hydride*	*Sulphur oxide*
$H=5{\cdot}915$	$H=11{\cdot}19\%$	$O=49{\cdot}95\%$
$S=94{\cdot}085$	$O=88{\cdot}81\%$	$S=50{\cdot}05\%$

In sulphur hydride,

5·915 grams of hydrogen combine with 94·085 grams of sulphur.

∴ 1 gram of hydrogen combines with $\frac{94{\cdot}085}{5{\cdot}915}=15{\cdot}91$ grams of sulphur.

In oxygen hydride,

11·19 grams of hydrogen unite with 88·81 grams of oxygen.

∴ 1 gram of hydrogen unites with $\frac{88{\cdot}81}{11{\cdot}19}=7{\cdot}936$ grams of oxygen

Hence, the ratio with which sulphur and oxygen combine with the same weight of hydrogen $=\frac{15{\cdot}91}{7{\cdot}936}=2{\cdot}004$

Now, in sulphur oxide,

50·05 grams of sulphur combine with 49·95 grams of oxygen.

Hence, the ratio with which sulphur and oxygen combine with each other is $\frac{50{\cdot}05}{49{\cdot}95}=1{\cdot}002$

Thus, the proportion by weight in which sulphur and oxygen combine with the same weight of hydrogen is twice the proportion by weight in which sulphur and oxygen combine with each other. Thus, the law of reciprocal proportions is proved.

Ex. 6. *1·5 grams of a metal gives 2·1 gram of its oxide. The carbonate of the metal contains 40% of the metal. Calculate with the help of the law of definite proportions the amount of the metal oxide which will be formed when 1 gram of the carbonate is completely decomposed to form the oxide.*

The weight of metal oxide $=2\cdot1$ grams.
The weight of the metal $=1\cdot5$ gram
$\therefore$ The weight of oxygen $=2\cdot1-1\cdot5=0\cdot6$ grams.

$$\text{Hence, in the metal oxide, } \frac{\text{weight of the metal}}{\text{weight of oxygen}}=\frac{1\cdot5}{0\cdot6}=\frac{5}{2}$$

Now, in 100 grams of metal carbonate 40 grams of metal are present.

$\therefore$ In 1 gram of metal carbonate $\frac{40}{100}=0\cdot4$ gram of the metal is present.

According to the law of definite proportions the ratio of the weight of the metal and oxygen will also be the same in the oxide obtained from metal carbonate. Hence,

In the oxide obtained from metal carbonate,

$$\frac{\text{weight of the metal}}{\text{weight of oxygen}}=\frac{5}{2} \quad \because \quad \frac{0\cdot4 \text{ gram}}{\text{Weight of oxygen}}=\frac{5}{2}$$

$\therefore$ Weight of oxygen $=\frac{2\times0\cdot4}{5}$ gram $=0\cdot16$ gram

$\therefore$ The weight of oxide obtained from 1 gram of the carbonate $=(0\cdot4+0\cdot16)=0\cdot56$ gram.

Ex. 7. *Two oxides of a metal M are heated to a constant weight in a stream of hydrogen. 1 gram of each oxide gave 0·12585 gram and 0·2264 gram of water respectively. Show that the results agree with the law of multiple proportions.* [H. S., '73]

From 1 gram of the first oxide 0·12585 gram of water is obtained. Now in 18 grams of water 16 grams of oxygen are present.

∴ 0·12585 gram of water $\frac{16\times0{\cdot}12585}{18}=0{\cdot}1119$ gram of oxygen is present.

∴ In the first oxide 0·1119 gram of oxygen is present.

∴ In the first oxide the amount of metal = 0·8881 gram

Hence 0·8881 gram of the metal combine with 0·1119 gram of oxygen.

∴ 1 gram of the metal combine with $\frac{0{\cdot}1119}{0{\cdot}8881}=0{\cdot}126$ gram of oxygen.

From 1 gram of the second oxide 0·2264 gram of water are formed.

Now, in 0·2264 gram of water the amount of oxygen present is $\frac{16\times0{\cdot}2264}{18}=0{\cdot}2013$ gram.

∴ In the second oxide the amount of the metal present
$=1-0{\cdot}2013=0{\cdot}7987$ gram.

∴ 0·7987 gram of the metal combine with 0·2013 gram of oxygen.

∴ 1 gram of the metal combines with $\frac{0{\cdot}2013}{0{\cdot}7987}=0{\cdot}252$ gram of oxygen.

∴ The different weights of oxygen which combine with the fixed weight of the metal are in the ratio 0·126 : 0·252 or 1 : 2. This is a ratio of small whole numbers. Hence, the data given in the problem illustrate the law of multiple proportions.

Ex. 8. *When 4 grams of each of the two oxides of the metal M are heated to a constant weight in a stream of hydrogen 0·5034 gram and 0·9056 gram of water are formed. If the formula of the second oxide be MO what will be the formula of the first oxide ?*

From 4 grams of the first oxide of the metal M, 0·5034 gram of water are formed.

Now, 18 grams of water contain 16 grams of oxygen.

0·5034 gram of water contain $\frac{16\times0{\cdot}5034}{18}=0{\cdot}4476$ gram of oxygen.

∴ In 4 grams of the first oxide 0·4476 gram of oxygen are present.

∴ Amount of metal present in the first oxide = 3·5524 gram.

Similarly, in 4 gram of the second oxide, the amount of oxygen present $= \frac{16 \times 0{\cdot}9056}{18} = 0{\cdot}8098$ gram.

∴ The amount of metal in the second oxide = 3·1902 grams.

Now the formula of the second oxide is MO.

Hence, $\frac{\text{the number of atoms of M}}{\text{the number of atoms of oxygen}} = \frac{1}{1} = \frac{3{\cdot}1902/A}{0{\cdot}8098/16}$

[A = the atomic weight of M]

∴ A = 63·03.

In the first oxide,

$$\frac{\text{the number of atoms of M}}{\text{the number of atoms of oxygen}} = \frac{3{\cdot}5524/63{\cdot}03}{0{\cdot}4476/16} = \frac{2}{1}$$

∴ The formula of the first oxide is M_2O.

Ex. 9. *Metal M and chlorine combine in different proportions to form two compounds A and B. The mass ratio M : Cl is 0·895 : 1 in A and 1·791 : 1 in B.*

(*a*) *which law of chemical combination does this law illustrate ?*

(*b*) *which of the following pairs of formula are correct on the basis of the above information alone.*

Compound A		**Compound B**
(*i*) MCl	*and*	M_2Cl
(*ii*) MCl	*and*	MCl_3
(*iii*) MCl_2	*and*	MCl
(*iv*) MCl_3	*and*	M_2Cl_3

[I. I. T., '69]

This example illustrates the law of multiple proportions.

In the first chloride, 1 part by weight of chlorine combines with 0·895 part by weight of the metal.

In the second chloride, 1 part by weight of chlorine combines with 1·791 part by weight of the metal.

∴ The different weights of the metal which combine with the fixed weight of chlorine are in the ratio $\frac{0{\cdot}895}{1{\cdot}791} = 1 : 2$. This is a simple ratio of small whole numbers. Hence the example illustrates the law of multiple proportions.

$$\text{Hence, } \frac{\text{the weight of M in B}}{\text{the weight of M in A}}=\frac{2}{1}$$

Hence A is MCl_2 and B is MCl

This ratio is present in (i), (iii) and (iv) but they are not acceptable since the valency of chlorine is 1.

Ex. 10. *Marsh gas contains 75% carbon and 25% hydrogen, carbonic oxide contains 42·86% carbon and 57·14% oxygen. Water contains 11·11% hydrogen and 88·88% oxygen. Show that the data illustrate the law of reciprocal proportions.*

In marsh gas,

75 grams of carbon combine with 25 grams of hydrogen.

$\therefore$ 1 gram of carbon combine with $\frac{25}{75}=\frac{1}{3}$ gram of hydrogen.

In carbonic oxide,

42·86 grams of carbon combine with 57·14 grams of oxygen.

$\therefore$ 1 gram of carbon combines with 1·333 grams of oxygen.

$\therefore$ The ratio (G) of the weights of hydrogen and oxygen which combine with the fixed weight of carbon is $0{\cdot}3333 : 1{\cdot}333 = 1 : 4$.

Now in water, the ratio by weight (H) in which hydrogen and oxygen combine is $11{\cdot}11 : 88{\cdot}88 = 1 : 8 = 1\times1 : 2\times4$

$$\text{or, } \frac{G}{H}=\frac{1/4}{1/8}=\frac{2}{1}$$

Therefore, these data illustrate the law of reciprocal proportions.

EXERCISE

I

1. State the law of definite proportions. Explain this law taking the compound AB_2 as an example ; the at. wt. of A is 118·7 and the at. wt. of B is 16.

Explain the law in the light of Dalton's atomic theory.

"The converse of the law of definite proportions is not true"—Explain with examples.

2. State the laws of chemical combination and explain each of them with an example.

3. State the law of multiple proportions and explain it with an example. Deduce the law from Dalton's atomic theory. "After the discovery of isotopes

some exceptions to the law of multiple proportions are observed."—Explain with examples.

4. State Dalton's atomic theory. Criticise it in the light of our present-day conceptions. Mention the usefulness of the theory.

5. State the law of reciprocal proportions and explain it with an example. Deduce the law from Dalton's atomic theory.

6. State the law of conservation of mass. Explain the law in the light of Dalton's atomic theory.

7. Give the definition of 'atom' according to Dalton. State the postulates of Dalton's atomic theory. How would you explain the law of definite proportions, the law of multiple proportions and the law of reciprocal proportions with the help of these postulates ?

What are the limitations of Dalton's atomic theory ?

8. State the law of gaseous volumes. Explain the law with an example.

9. What is the law of conservation of mass-energy ? Explain how heat is evolved or absorbed in chemical reactions. What mass in gram is equivalent to 10 calories of heat ?

10. Verify the law of conservation of mass with the help of two experiments. How will you verify the law of multiple proportions ?

II

11. An element forms two different compounds with oxygen. In the first compound, the per cent of the element by weight is 81·6 and in the second compound the per cent of the element by weight is 59·7. Show that the results are in agreement with the law of multiple proportions.

12. A metal forms two oxides. When 1 gram of each oxide is reduced by carbon, 0·8815 and 0·7881 gm. of the metal are obtained. Show how these results illustrate the law of multiple proportions.

If the formula of the first oxide be MO, what is the formula of the second oxide ? [Ans. MO_2.]

13. 2·2 grams of carbon dioxide are evolved by reducing 8 grams of copper oxide by carbon. If the composition of carbon dioxide is characterised by the ratio 3 : 8, i.e., 3 weight parts of carbon per 8 weight parts of oxygen, calculate the composition of copper oxide. [Ans. (Cu) : (O)=4 : 1.]

14. A metal M forms two oxides. When 1 gram of the oxide A is heated to a constant weight in a stream of hydrogen, 0·12585 gram of water is formed. 1 gram of the oxide B similarly gave 0·2264 gram of water. If the formula of the oxide B is given by MO, what is the formula of the oxide A ? [Calcutta, 1951]
[Ans. M_2O]

15. How many grams of water will be formed on burning 20 grams. of hydrocarbon containing 25 per cent of hydrogen and 75 per cent of carbon ? The composition of water is expressed by the ratio (H) : (O)=1 : 8. [Ans. 45 grams.]

16. The percentage composition of ammonia is : H=17.76%,
N=82.24%. When 3·77 grams of hydrogen react completely with 26·23

grams of nitrogen, 30·000 grams of hydrazine are formed. Show that these data are in agreement with the law of multiple proportions.

17. An element M forms two oxides. In one gram of the oxide A there is $\frac{3}{7}$ gram of the element and in one gram of the oxide B, there is $\frac{3}{11}$ gram of element. If the formula of the oxide A is MO, deduce the formula of the oxide B. [Ans. MO_2]

18. Show that the following data are in agreement with the law of reciprocal proportions.

Methane		Carbon monoxide		Water	
Carbon	75%	Carbon	42·86%	Hydrogen	11·11%
Hydrogen	25%	Oxygen	57·14%	Oxygen	88·89%

[Nagpur, 1935]

19. Illustrate the law of reciprocal proportions using the following data :

Nitrogen hydride	Oxygen hydride	Nitrogen oxide
H = 17·76%	H = 11·19%	O = 63·14%
N = 82·24%	O = 88·81%	N = 36·86%

20. On burning 16 grams of cupric sulphide (containing 80 per cent of copper and 20 per cent of sulphur), 16 grams of copper oxide and 6·4 grams of sulphur dioxide were obtained. Determine the composition of copper oxide and sulphur dioxide and express their ratio with the least whole number.

[Ans. In copper oxide, % Cu = 80, %O = 20
(Cu) : (O) = 1 : 4, (S) : (O) = 1 : 1
In sulphur oxide, %S = 50, %O = 50.]

21. Ethylene contains 85·71% carbon, and 14·29% hydrogen and carbon dioxide contains 27·27% carbon and 72·73% oxygen. Water contains 11·11% hydrogen and 88·89% oxygen. Show that the results illustrate a law of chemical combination. State the law.

22. Potassium chloride contains 52·5% potassium and 47·5% chlorine and potassium iodide contains 23·6% potassium and 76·4% iodine. Iodine chloride contains 78·2% iodine and 21·8% chlorine. Show that the results illustrate a law of chemical combination. State the law.

23. Nitrogen forms two oxides. The percentage composition of the oxides are given below :

(a) Nitrogen = 63·63% Oxygen = 36·36%
(b) Nitrogen = 46·66% Oxygen = 53·33%

Show that the data illustrate the law of multiple proportions.

24. Iron forms two oxides. The first oxide contains 69·34% iron and 30·66% oxygen. The second oxide contains 77·22% iron and 22·78% oxygen. Show that the data illustrate a law of chemical combination. State the law.

25. Phosphine contains 91·1% phosphorus, and 8·9% hydrogen ; water contains 88·8% oxygen and 11·2% hydrogen and phosphorus trioxide (P_2O_3) contains 56·4% phosphorus and 43·6% oxygen. Without using atomic weights show that the results illustrate the law of reciprocal proportions.

26. 0·46 gram of magnesium gives 0·77 gram of magnesium oxide (MgO), 0·81 gram of magnesium displaces 760 c.c. of hydrogen at N.T.P. from an acid. 0·08 gram of oxygen produces 0·09 gram of water. Show that these data illustrate a law of chemical combination. State the law.

Amount of oxygen in magnesium oxide $= 0{\cdot}77 - 0{\cdot}46 = 0{\cdot}31$ gram

∴ 0·46 gram of magnesium combine with 0·31 gram of oxygen.

∴ 1 gram of magnesium combine with $\frac{0{\cdot}31}{0{\cdot}46} = 0.674$ gram of oxygen.

Now 1 c.c. of hydrogen weigh at N.T.P. 0·00009 gram

∴ 760 c.c. of hydrogen weigh at N.T.P. $0{\cdot}00009 \times 760$ or, 0·0684 gram.

∴ 0·81 gram of magnesium displaces 0·0684 gram of hydrogen from an acid.

∴ 1 gram of magnesium displaces $\frac{0{\cdot}0684}{0{\cdot}81} = 0{\cdot}0844$ gram of hydrogen.

The weights of hydrogen and oxygen which combine with the fixed weight of magnesium are in the ratio $0{\cdot}0844 : 0{\cdot}674 = 1 : 8$

Now 0·09 gram of water contains 0·08 gram of oxygen. Hence the amount of hydrogen present in 0·09 gram of water is $0{\cdot}09 - 0{\cdot}08 = 0{\cdot}01$ gram. Therefore hydrogen and oxygen combine with one another in the ratio $0{\cdot}01 : 0{\cdot}08 = 1 : 8$.

Hence the results illustrate the law of reciprocal proportions.

27. 2·07 gram of a metal form 2·23 gram of oxide. The nitrate of the metal contains 62·53% metal.

Calculate with the help of the law of definite proportion the amount of oxide formed when 1 gram, of the nitrate is heated. [Ans. 0·673 gram.]

28. Three samples of silver chloride are collected from three different sources : (a) 130·602 gram. of silver chloride contain 98·314 gram of silver. (b) 530·92 grams of silver chloride contain 399·651 grams of silver. (c) 144·207 grams of silver chloride contain 108·549 grams of silver. Which law of chemical combination is illustrated by these data ?

29. Two chlorides of a metal contain 35·9% and 52·8% chlorine respectively. Show that the results illustrate the law of multiple proportions.

[H. S. (Comp.), '63, '66]

30. Two samples of lead sulphide are collected from two different sources. After analysis the following results are obtained :

(a) 28·855 grams of lead sulphide contain 25 grams of lead.

(b) 17·3125 grams of lead sulphide contain 15 grams of lead.

Which law of chemical combination is illustrated by these results ?

31. The elements A and B form three compounds. The first compound contains 75% A and 25% B. The second compound contains 80% A and 20% B and the third compound contains 85·7% A and 14·3% B. Show that the results are in agreement with the law of multiple proportions.

32. After the analysis of three oxides of lead the following results are obtained : The first oxide contains 7·15% oxygen, the second oxide contains 9·37% oxygen and the third oxide contains 13·49% oxygen. Show that these results are in agreement with the law of multiple proportions.

33. 5·6 grams of calcium oxide contain 1·6 gram of oxygen. Calcium carbonate contains 40% calcium. Calculate with the help of the law of definite proportion the amount of calcium oxide when 2 grams of calcium carbonate are heated. [Ans. 1·12 gram]

34. Ferrous sulphide contains 36·47% sulphur. Calculate the amount of ferrous sulphide formed when 4 grams of iron are heated with 11 grams of sulphur. What amount of sulphur will remain unreacted ?

[Ans. 6·296 grams ; 8·704 grams]

35. 4 gram of calcium form 5·6 grams of calcium oxide. 1 gram of calcium displaces 560 c.c. of hydrogen at N.T.P. from an acid. 0·8 gram of oxygen combines with hydrogen to give 0·9 gram of water. Show that these results illustrate a law of chemical combination.

36. One gram of each of the two oxides of the metal M are heated to a constant weight in a stream of hydrogen. The first oxide gives 0·12585 gram of water and the second oxide gives 0·2264 gram of water. Show that the results illustrate a law of chemical combination.

CHAPTER IV

ATOMS AND MOLECULES

4·1. Barzelius's hypothesis. According to Dalton's atomic theory, "elements combine in simple ratio by atoms." Again, according to Gay-Lussac's law, gases combine in simple ratio by volume. The Swedish chemist, Berzelius, made a first attempt to explain the experimental results of Gay-Lussac. He correlated the law of combining volumes and the Dalton's atomic theory in a hypothesis which may be stated as:

Equal volumes of all gases under the same conditions of temperature and pressure contain the same number of atoms.

But when this hypothesis of Barzelius was applied to explain the experimental facts, it led to a conclusion which was in direct conflict with the fundamental postulate of the atomic theory that atoms cannot be divided. For example, in the reaction: hydrogen + chlorine = hydrogen chloride, it is found by experiment that

1 volume of hydrogen combines with 1 volume of chlorine to yield 2 volumes of hydrogen chloride.

Let n be the number of atoms present in 1 volume of hydrogen. Then by Berzelius's hypothesis, n atoms of chlorine are also present in 1 volume of chlorine and 2n atoms are present in 2 volumes of hydrogen chloride. Hence, we get

n atoms of hydrogen combine with n atoms of chlorine to yield 2n complex atoms of hydrogen chloride.

∴ 1 atom of hydrogen combines with 1 atom of chlorine to yield 2 complex atoms of hydrogen chloride.

or, $\frac{1}{2}$ atom of hydrogen combines with $\frac{1}{2}$ atom of chlorine to yield 1 complex atom of hydrogen chloride.

That is, in forming 1 complex atom of hydrogen chloride, $\frac{1}{2}$ atom of hydrogen reacts with $\frac{1}{2}$ atom of chlorine. This means that each atom of hydrogen and each atom of chlorine must have been divided into two portions. This is contrary to the Dalton's atomic theory that atoms are particles of matter which cannot be subdivided by chemical processes. Hence, if the Dalton's atomic theory is to be retained, the hypothesis of Berzelius must be regarded as false.

The key to the explanation of Gay-Lussac's law was found by Italian physicist, Amadeo Avogadro. Avogadro in 1811 pointed out that all these contradictions could easily be eliminated by introducing the conception of the "molecule" which he regarded as a cluster of small number of atoms. He further regarded the molecule as the smallest particle of any substance capable of independent existence, and at the same time retained the conception of the atom as the smallest amount of an element in molecules of various compounds. Consequently, the smallest unit of matter which can exist in free state in a gas is not an atom but a molecule. Hence, a relation exists between the volumes of a gas and the number of molecules present in it. This relation is expressed by Avogadro's hypothesis.

Fig. 4.1 : Amadeo Avogadro.

4·2. Avogadro's hypothesis. Avogadro's hypothesis may be stated : *Equal volumes of all gases under the same conditions of temperature and pressure contain the same number of molecules.*

Avogadro's hypothesis explained successfully the simple proportions between the volumes of reacting and resulting gases. Two reactions may be considered as examples :

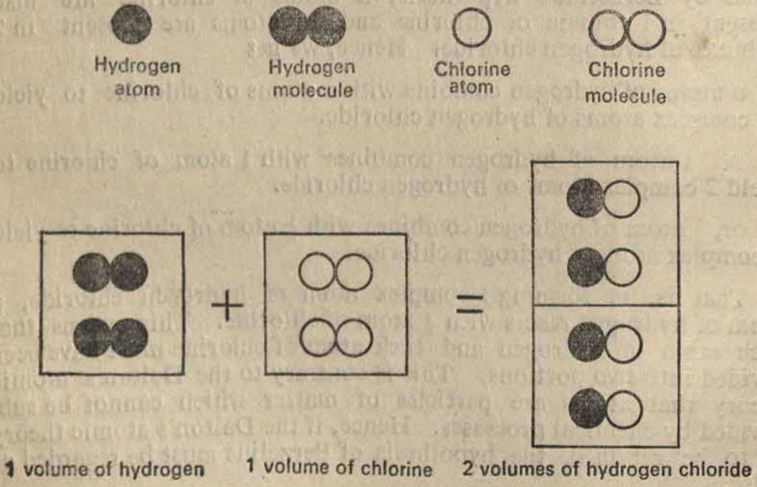

Fig. 4.2

(i) The reaction : hydrogen+chlorine=hydrogen chloride

1 vol. + 1 vol. =2 vols.

Experimentally, it is found that 1 volume of hydrogen unites with 1 volume of chlorine to yield 2 volumes of hydrogen chloride.

Let n be the number of molecules present in 1 volume of hydrogen. Hence, by Avogadro's hypothesis n molecules of hydrogen unite with n molecules of chlorine to yield 2n molecules of hydrogen chloride. Or, 1 molecule of hydrogen unites with 1 molecule of chlorine to yield 2 molecules of hydrogen chloride. Or, $\frac{1}{2}$ molecule of hydrogen unites with $\frac{1}{2}$ molecule of chlorine to yield 1 molecule of hydrogen chloride.

This is not in contradiction with the Dalton's atomic theory because molecules can be broken down in a chemical reaction into its constituent atoms. In this chemical reaction, the atoms in the molecules of hydrogen and chlorine have re-associated to form new molecules of hydrogen chloride, but no atom has been subdivided.

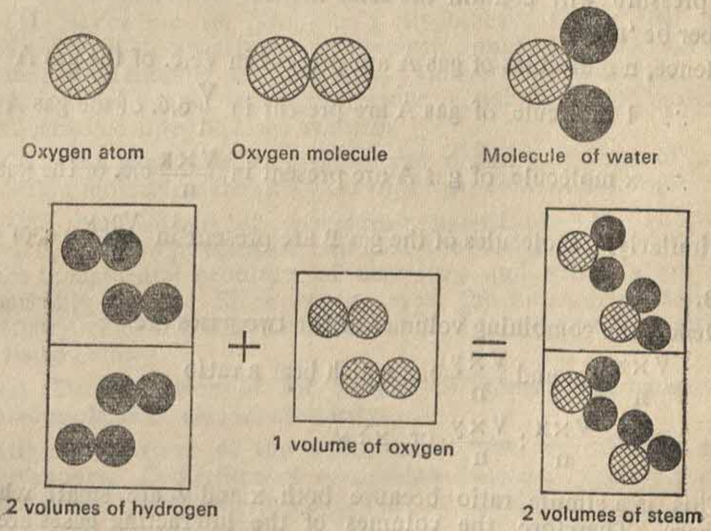

Fig. 4.3

(2) The reaction : hydrogen + oxygen = steam
2 vols. + 1 vol. = 2 vols.

It is found experimentally that 2 volumes of hydrogen combine with 1 volume of oxygen to form 2 volumes of steam.

Let *n* be the number of molecules present in 1 volume of oxygen. Then by Avogadro's hypothesis, 2n molecules of hydrogen combine with n molecules of oxygen to form 2n molecules of steam.

Or, 2 molecules of hydrogen combine with 1 molecule of oxygen to form 2 molecules of steam.

Or, 1 molecule of hydrogen combines with $\frac{1}{2}$ molecule of oxygen to form 1 molecule of steam.

This, again, is not in contradiction with the atomic theory, since the molecule of oxygen can be split up into its constituent atoms. The atoms in the molecule of hydrogen and oxygen re-associate to form the new molecule of steam but no atom undergoes subdivision.

4.3. Deduction of Gay-Lussac's law of combining volumes from Avogadro's hypothesis. The law of combining volumes can be deduced from Avogadro's hypothesis as follows :

Let us consider a reaction in which x molecules of the gas A unite with y molecules of the gas B to form a compound of A and B, where x and y are small whole numbers. By Avogadro's hypothesis, Vc.c. of each gas under the same conditions of temperature and pressure will contain the same number of molecules. Let the number be 'n'.

Hence, n molecules of gas A are present in Vc.c. of the gas A

$\therefore$ 1 molecule of gas A are present in $\frac{V}{n}$ c.c. of the gas A

$\therefore$ x molecule of gas A are present in $\frac{V \times x}{n}$ c.c. of the gas A

Similarly, y molecules of the gas B are present in $\frac{V \times y}{n}$ c.c. of the gas B.

Hence, the combining volumes of the two gases are

$\frac{V \times x}{n}$ c.c. and $\frac{V \times y}{n}$ c.c. which bear a ratio

$$\frac{V \times x}{n} : \frac{V \times y}{n} \text{ or } x : y.$$

This is a simple ratio because both x and y are small whole numbers. Therefore, the volumes of the interacting gases are in a ratio of small whole numbers to one another, which is Gay-Lussac's law.

4.4. Modification of Dalton's atomic theory. Avogadro's conception of molecules revolutionised the concept about the structure of matter. Avogadro's hypothesis explained remarkably well the Gay-Lussac's law of combining volumes which stood in apparent contradiction with the Dalton's atomic theory. Consequently, the atomic theory of Dalton was modified. The modification involved the introduction of the Avogadro's conception of molecules and the distinction between the atoms and molecules. These two most important conceptions of chemistry, i.e., atoms and molecules were distinguished as :

A molecule is the ultimate particle of a substance which can exist in the free state. The molecules are composed of indivisible particles called atoms. The properties of a substance are the properties of its molecule. When a molecule of a substance is broken down, the essential chemical properties of the substance are lost.

An atom is the smallest particle of an element which can take part in a chemical change. An atom cannot exist in the free state. When two or more substances react chemically, the molecules of the substances are split up into atoms which then combine together in simple numerical proportions to form the molecules of new substances.

Two axiomatic facts from Avogadro's hypothesis.

(1) According to Avogadro's hypothesis, under the same conditions of temperature and pressure equal volumes of all gases contain equal number of molecules. Conversely, under the same conditions of temperature and pressure, equal number of molecules of all gases occupy the same volume.

(2) At a particular temperature and pressure, if vc.c. of a gas contain n molecules, then $a \times$ v c.c of the gas contain $a \times$ n molecules.

4.5. Applications of Avogadro's hypothesis. In 1858, Cannizzaro, an Italian scientist, applied the Avogadro's hypothesis to the fundamental problems of chemistry and solved them with remarkable clarity. Some of the most fundamental problems of chemistry which can be solved successfully by Avogadro's hypothesis are listed below :

(i) Determination of the number of atoms in the molecule of a gaseous element, i.e., its atomicity.

(ii) Comparison of the molecular weights of different gases and vapours. Deduction of a relation between the molecular weight of any gas or vapour and its vapour density.

(iii) Establishment of the fact that the gram-molecular weight of any gas occupies 22·414 litres at N. T. P.

(iv) Determination of the molecular formula of a gas from its volumetric composition.

(v) Determination of the atomic weights of the elements.

(vi) Determination of molecular weights.

(i) Determination of the number of atoms in the molecule of a gaseous element, i.e., the atomicity of gaseous elements.

(a) Experimentally, we find that 1 volume of hydrogen combines with 1 volume of chlorine to yield 2 volumes of hydrogen chloride.

Let n be the number of molecules present in 1 volume of hydrogen. Then by Avogadro's hypothesis,

n molecules of hydrogen combine with n molecules of chlorine to yield 2n molecules of hydrogen chloride.

or, 1 molecule of hydrogen combines with 1 molecule of chlorine to yield 2 molecules of hydrogen chloride.

or, $\frac{1}{2}$ molecule of hydrogen combines with $\frac{1}{2}$ molecule of chlorine to yield 1 molecule of hydrogen chloride.

The molecule of hydrogen must split, therefore, into two equal parts. But since the atom is the smallest particle of matter, it follows that the molecule of hydrogen cannot contain less than 2 atoms.

Again, hydrogen chloride is a compound of hydrogen and chlorine. Therefore, one molecule of hydrogen chloride must contain at least one atom of hydrogen and one atom of chlorine, which come from $\frac{1}{2}$ molecule of hydrogen and $\frac{1}{2}$ molecule of chlorine. Since atom is the smallest particle of matter, it follows that a molecule of hydrogen or chlorine must contain at least two atoms.

Again, if we allow metallic sodium to act on hydrogen chloride, hydrogen present in hydrogen chloride is replaced by sodium and sodium chloride is formed. No more hydrogen is replaced from sodium chloride by any means. Thus, hydrogen is replaced from hydrogen chloride in one stage and not in two stages. Hence, the molecule of hydrogen chloride contains only 1 atom of hydrogen. This 1 atom of hydrogen comes from $\frac{1}{2}$ molecule of hydrogen. Hence, 1 molecule of hydrogen contains 2 and only 2 atoms of hydrogen.

(b) In the same way, we can show that the molecule of oxygen contains at least 2 atoms. Experimentally, we find that 2 volumes of hydrogen unite with 1 volume of oxygen to form 2 volumes of steam.

Let n be the number of molecules present in 1 volume of oxygen. Then by Avogadro's hypothesis,

2n molecules of hydrogen unite with n molecules of oxygen to form 2n molecules of steam.

or, 2 molecules of hydrogen unite with 1 molecule of oxygen to form 2 molecules of steam.

or, 1 molecule of hydrogen unites with $\frac{1}{2}$ molecule of oxygen to form 1 molecule of steam.

But 1 molecule of steam must contain at least 1 atom of oxygen. This 1 atom of oxygen comes from $\frac{1}{2}$ molecule of oxygen and hence 1 molecule of oxygen must contain at least two atoms.

The number of atoms in 1 molecule of any substance is defined as its *atomicity*. Hydrogen has two atoms in 1 molecule and is diatomic and we assign to 1 molecule of hydrogen the formula, H_2. Similarly, it has been concluded that the molecules of the gases, oxygen, nitrogen, and chlorine, are also diatomic and we assign to them the formulas O_2, N_2, Cl_2, respectively.

That the molecules of hydrogen, oxygen, nitrogen, and chlorine are diatomic, has also been established by a purely physical method, namely, by measuring the ratio of the specific heats at constant pressure and at constant volume. The kinetic theory of gases gives the value of the ratio as 1·66 for monatomic gases and 1·40 for diatomic gases. The ratios for hydrogen, oxygen, nitrogen and chlorine have been found experimentally to be 1·41, 1·40, 1·40, and 1·34 respectively. Hence, these gaseous elements are diatomic.

Atomicity of the gaseous elements is not always 2. Mercury vapour and argon are monatomic, ozone (O_3) is triatomic, phosphorus and arsenic vapour are tetratomic (P_4, As_4).

Density. The density of a substance is its mass per unit volume. If the mass of a substance is m and its volume is v, then its density is given by $d=\frac{m}{v}$.

The density obtained by expressing the mass in grams and the volume it occupies in c.c or millilitres is called the *absolute density* or simply the density,

$$\text{Absolute density or density}=\frac{\text{mass of the substance in grams}}{\text{volume of the substance in c.c.}}$$

$$=\frac{\text{m gram}}{\text{V c.c.}}$$

Hence, the unit of absolute density is gram/c.c.

The volume of a substance changes with temperature and pressure but its mass remains unchanged. Hence, the absolute density of a substance depends on its temperature and pressure. The mass of a given volume of a gas is small in comparison with the mass of the same volume of a liquid or a solid. Again, the volume of a gas is highly dependent on temperature and pressure. For this reason, the density of a gas cannot be expressed in absolute density defined above. Under standard conditions or at 0°C and 760 mm. pressure the mass of 1 litre of a gas is called *normal density*. The normal density of hydrogen is 0·0899 gm./litre or the mass of 1 litre of hydrogen at N.T.P. is 0·0899 gram. The unit of normal density is gram/litre.

In order to make density unitless or to express density in pure numbers, the density of a gas or vapour is expressed by comparing with the density of hydrogen at the same temperature and pressure. This is called *relative density* or *vapour density*.

The relative density or vapour density of a gas or vapour is the ratio of the weight of a given volume of the gas to the weight of an equal volume of hydrogen measured under the same conditions of temperature and pressure. Hydrogen is taken as the standard because it is the lightest gas known. Hence we have,

The vapour density of a gas (H=1)

$$= \frac{\text{weight of Vc.c. of the gas}}{\text{weight of Vc.c. of hydrogen}}$$

(at the same temperature and pressure)

$$= \frac{\text{weight of 1 c.c. of the gas}}{\text{weight of 1 c.c. of hydrogen}}$$

(at the same temperature and pressure)

The vapour density of sulphur dioxide

$$= \frac{\text{weight of Vc.c. of sulphur dioxide}}{\text{weight of Vc.c. of hydrogen}}$$

(at the same temperature and pressure)

$$= \frac{\text{weight of 1 c.c. of sulphur dioxide}}{\text{weight of 1 c.c. of hydrogen}}$$

(at the same temperature and pressure)

$= 32$ (by experiment)

Hence, at the same temperature and pressure 1 c.c. of sulphur dioxide is 32 times heavier than 1 c.c. of hydrogen

Now, the vapour density of a gas

$$= \frac{\text{weight of 1 litre of the gas at N.T.P.}}{\text{weight of 1 litre of hydrogen at N.T.P.}}$$

$$= \frac{\text{Normal density of the gas}}{\text{Normal density of hydrogen}}$$

$$= \frac{\text{Normal density of the gas}}{0{\cdot}09}$$

∴ The normal density of a gas = vapour density of the gas × 0·09.

Hence, the mass of 1 litre of the gas at N.T.P.

= its vapour density × 0·09.

The vapour density has no unit. It is a pure number.

If oxygen is taken as the standard instead of hydrogen, i.e., on oxygen standard the vapour density of a gas is given by

vapour density of a gas (O=1)

$$= \frac{\text{weight of Vc.c. of the gas}}{\text{weight of Vc.c. of oxygen}}$$

(at the same temperature and pressure).

Similarly, if chlorine is taken as the standard, i.e., on chlorine standard, the relative density of a gas is defined as :

The relative density of a gas (Cl = 1)

$$=\frac{\text{weight of Vc.c. of the gas}}{\text{weight of Vc.c. of chlorine}}$$

(at the same temperature and pressure)

In this way, the relative density of a gas is expressed on different standards. The relationship between relative densities on different standards are found out as follows :

The relative density of a gas (H = 1)

$$=\frac{\text{weight of Vc.c. of the gas}}{\text{weight of Vc.c. of hydrogen}}$$

(at the same temperature and pressure)

$$=\frac{\text{weight of Vc c. of the gas}}{\text{weight of Vc.c. of oxygen}}\times\frac{\text{weight of Vc.c. of oxygen}}{\text{weight of Vc.c. of hydrogen}}$$

$$=\text{the vapour density of the gas }(O=1)\times\text{vapour density of oxygen }(H=1)$$

$\therefore$ The vapour density of a gas (O = 1)

$$=\frac{\text{vapour density of the gas }(H=1)}{\text{vapour density of oxygen }(H=1)}$$

$\therefore$ The vapour density of a gas (O = 1)

$$=\frac{\text{vapour density of the gas }(H=1)}{16}$$

Similarly, the vapour density of a gas (Cl = 1)

$$=\frac{\text{vapour density of the gas }(H=1)}{\text{vapour density of chlorine }(H=1)}$$

$$=\frac{\text{vapour density of the gas }(H=1)}{35{\cdot}5}$$

(ii) The relation between molecular weight and relative density.

The relative density (also called vapour density) of a gas or vapour is the ratio of the weight of a given volume of the gas to the weight of an equal volume of hydrogen measured under the same conditions of temperature and pressure. Hydrogen is taken as the standard because it is the lightest gas known. By definition, we have :

Relative density

$$=\frac{\text{weight of a given volume of the gas}}{\text{weight of an equal volume of hydrogen}}\quad\text{(at the same temperature and pressure)}$$

$$=\frac{\text{weight of Vc.c. of the gas}}{\text{weight of Vc.c. of hydrogen}}\quad\text{(at the same temperature and pressure)}$$

Let n be the number of molecules present in Vc.c. of the gas. Hence, by Avogadro's hypothesis, Vc.c. of hydrogen will also contain 'n' number of molecules.

$$\text{Therefore, relative density} = \frac{\text{weight of n molecules of the gas}}{\text{weight of n molecules of hydrogen}}$$

$$= \frac{\text{weight of 1 molecule of the gas}}{\text{weight of 1 molecule of hydrogen}}$$

$$= \frac{\text{molecular weight of the gas}}{\text{molecular weight of hydrogen}}$$

Now, it has been shown that a molecule of hydrogen contains two atoms. The atomic weight of hydrogen is 1 and hence its molecular weight is 2. Therefore, we have

$$\text{Relative density} = \frac{\text{Molecular weight of the gas}}{2}$$

Hence, molecular weight $= 2 \times$ relative density.

Multiplication of the relative density of a gas by 2, therefore, gives its molecular weight.

Actually, on the atomic weight standard, carbon $= 12$, the atomic weight of hydrogen is 1·008 and hence the molecular weight of hydrogen is 2·016 instead of 2. So where absolute accuracy is required, the molecular weight is obtained from the relation :

Molecular weight $= 2{\cdot}016 \times$ relative density.

(iii) Gram-molecular weight and gram-molecular volume or molar volume.

In chapter II, it was pointed out that the molecular weight of any gas expressed in grams is its gram-molecular weight. The gram-molecular weight unit is also referred to as the mole. If we wish to use 2 moles of water in a chemical reaction, we must weigh out 36 grams (i.e., 2×18 grams, 18 is the molecular weight of water) of water. Hence, the number of moles represented by a weight in grams of a substance is given by the relation,

$n = \frac{g}{M}$ where n = number of moles, g = weight in grams and M = molecular weight in grams.

The volume occupied by a mole or gram-molecular weight of a substance is called the molar volume or gram-molecular volume.

(a) Molar volume of all gases is the same at the same temperature and pressure. Let us suppose that

molecular weight of a substance $= M$

the absolute weight of a hydrogen atom $= a$ gram

$\therefore$ the weight of 1 gram-molecule of the substance $= M$ gram, By definition of molecular weight, molecular weight of a substance, M

$$=\frac{\text{weight of 1 molecule of the substance}}{\text{weight of 1 atom of hydrogen}}$$

$$\therefore\quad M=\frac{\text{weight of 1 molecule of the substance}}{a}$$

$\therefore$ weight of 1 molecule of the substance $= M \times a$ gram.

Now, weight of 1 gram-molecule of the substance $=$ M gram

Number of molecules of the substance present in its 1 gram-molecule $=\frac{M}{M\times a}=\frac{1}{a}$.

Since a is the weight of 1 molecule of hydrogen, $\frac{1}{a}$ is a constant quantity. Hence, the number of molecules of any substance present in its 1 gram-molecule is the same.

For example, the vapour density of ammonia $= 8{\cdot}5$

$\therefore$ Molecular weight of ammonia $= 8{\cdot}5\times 2 = 17$

$\therefore$ 1 gram-molecule of ammonia $= 17$ gram

Now, the weight of one atom of hydrogen $= a$ gram

1 molecule of ammonia is 17 times heavier than 1 atom of hydrogen.

$\therefore$ weight of 1 molecule of ammonia $= 17a$ gram

$\therefore$ The number of molecules of ammonia present in its 1 gram-molecule $=\frac{17 \text{ gram}}{17a \text{ gram}}=\frac{1}{a}$.

Hence, in 1 gram-molecule of all substances is present the same number of molecules. Since according to Avogadro's law, the same number of molecules of different gases occupy the same volume at the same temperature and pressure, the volume of 1 gram-molecule or molar volume of all substances in the gaseous state is the same. That is, at the same temperature and pressure, molar volume of all gases is the same.

(b) Molar volume of all gases is 22·4 litres at N.T.P. It is found experimentally that 1 litre of hydrogen weighs nearly 0·09 gram at N.T.P. Now, by the definition of relative density we have

$$\text{relative density of a gas}=\frac{\text{Weight of 1 litre of the gas at N. T. P.}}{\text{Weight of 1 litre of hydrogen at N.T.P.}}$$

$$\therefore\quad \frac{M}{2{\cdot}016}=\frac{\text{Weight of 1 litre of the gas at N. T. P.}}{0{\cdot}09}$$

where M is the molecular weight of the gas. If the molecular weight is expressed in gram, we have

$$\frac{\text{M grams}}{2{\cdot}016}=\frac{\text{Weight of 1 litre of the gas at N. T. P. in grams}}{0{\cdot}09 \text{ grams}}$$

or, $\frac{\text{M grams}\times 0{\cdot}09}{2{\cdot}016}$ = Weight of 1 litre of the gas at N. T. P.

Therefore, $\frac{\text{M}\times 0{\cdot}09}{2{\cdot}016}$ grams of the gas occupy 1 litre at N. T. P.

∴ M grams of the gas occupy $\frac{2{\cdot}016\times 1}{0{\cdot}09}$ litre = 22·4 litres at N. T. P.

or, 1 mole of the gas occupies 22·4 litres at N. T. P.

Hence, the molar volume or gram-molecular volume of all gases at N. T. P. is 22·4 litres.

The volumes occupied by one mole of some gases at N. T. P. are given in table 4.1.

Table 4.1

Formula	1·00 mole	Weight of 1 litre (in grams)	Volume in litres per mole or molar volume
H_2	2·016 grams	0·0899	$\frac{2{\cdot}016}{0{\cdot}0899}=22{\cdot}42$
O_2	32·00 grams	1·429	$\frac{32}{1{\cdot}429}=22{\cdot}39$
CO_2	44·01 grams	1·977	$\frac{44{\cdot}01}{1{\cdot}977}=22{\cdot}26$
HCl	36·47 grams	1·639	$\frac{36{\cdot}47}{1{\cdot}639}=22{\cdot}25$

From the data given in table 4.1, it is evident that the conclusion that molar volume of all gases is the same at the same temperature and pressure and is equal to 22·4 litres at N. T. P., is only approximately correct.

Relation between molecular weight and normal density. Let M be the molecular weight of a gas, and ρ be the normal density in gram/litre. Then the weight of one litre of the gas at N.T.P. = ρ gram.

Therefore, the volume of one mole of the gas at N.T.P. = $\frac{M}{\rho}$ litre = 22·4 litre.

$$\therefore \quad \frac{M}{\rho}=22{\cdot}4 \qquad \therefore \quad M=\rho\times 22{\cdot}4$$

The Avogadro number and the mole. By Avogadro's hypothesis, it has been proved that gram-molecular volume or molar volume of all gases is the same at the same temperature and pressure and is equal to 22·4 litres at N. T. P. Since equal volumes of all gases under the same conditions of temperature and pressure contain the same number of molecules, it follows that one molar volume of all gases contains the same number of molecules. In other words, one mole or one gram-molecular weight of any substance contains the same number of molecules. This number has been determined by various methods to be $6{\cdot}023 \times 10^{23}$. This number is known as the *Avogadro number* and is designated by N. Hence one gram-molecule of nitrogen or 28 grams of nitrogen contain $6{\cdot}023 \times 10^{23}$ nitrogen molecules ; one gram-molecule of oxygen or 32 grams of oxygen contain $6{\cdot}023 \times 10^{23}$ oxygen molecules ; one gram-molecule of ammonia or 17 grams of ammonia contain $6{\cdot}023 \times 10^{23}$ ammonia molecules and one gram-molecule of carbon dioxide or 44 grams of carbon dioxide contain $6{\cdot}023 \times 10^{23}$ carbon dioxide molecules. Therefore, it follows that one gram-molecule of any substance contains Avogadro number of molecules or $6{\cdot}023 \times 10^{23}$ molecules of that substance. For this reason, 1 gram-molecule of a substance is called *a mole of molecules* of that substance.

Again, one gram-atom of any substance contains Avogadro number of atoms or $6{\cdot}023 \times 10^{23}$ atoms of that substance. For this reason, one gram-atom of a substance is called *a mole of atoms* of that substance. For example, one mole of sulphur atoms or 32 grams of sulphur (atomic weight of sulphur=32) contain $6{\cdot}023 \times 10^{23}$ sulphur atoms and one mole of chlorine atoms or 35·453 grams of chlorine contain $6{\cdot}023 \times 10^{23}$ chlorine atoms.

Similarly, 1 Faraday of electricity contains Avogadro number of electrons or $6{\cdot}023 \times 10^{23}$ electrons. Hence, 1 Faraday of electricity is called 1 mole of electrons.

Thus we see that a mole of an object means Avogadro number of objects or $6{\cdot}023 \times 10^{23}$ objects just as a dozen of objects means 12 objects. Hence a mole of molecules of a substance means Avogadro number of molecules or $6{\cdot}023 \times 10^{23}$ molecules of that substance ; a mole of atoms of a substance means Avogadro number of atoms or $6{\cdot}023 \times 10^{23}$ atoms of that substance and a mole of electrons means Avogadro number of electrons or $6{\cdot}023 \times 10^{23}$ electrons. Hence, *a mole means a collection of Avogadro number of objects or* $6{\cdot}023 \times 10^{23}$ *objects.*

It has been mentioned earlier that there are Avogadro number of molecules present in 1 gram-molecular weight of any substance. Conversely, the weight of Avogadro number of molecules of a substance is the gram-molecular weight of the substance. In other words, the weight of 1 mole of molecules of a substance is the gram-molecular weight of the substance. Similarly, the weight of 1 mole of atoms of an element is the gram-atomic weight of the element.

We can also choose to express mass in pounds instead of grams. In that case, one pound-molecular weight of all substances will contain the same number of molecules but this number will be different from Avogadro number given above. For example, 32 pounds of oxygen and 28 pounds of nitrogen will contain the same number of molecules but this number is different from the Avogadro number mentioned above. Since 1 pound is equal to 453 grams, this number can be calculated as follows :

32 grams of oxygen contain $6{\cdot}023 \times 10^{23}$ molecules.

$\therefore$ 453 grams of oxygen contain $\dfrac{6{\cdot}023 \times 10^{23} \times 453}{32}$ molecules

or, 1 pound of oxygen contain $\dfrac{6{\cdot}023 \times 10^{23} \times 453}{32}$ molecules

or, 32 pounds of oxygen contain $\dfrac{6{\cdot}023 \times 10^{23} \times 453 \times 32}{32}$

$= 2{\cdot}73 \times 10^{26}$ molecules.

Thus we see that if mass is expressed in grams in the definition of mole and the Avogadro number, the term gram-mole is used. If mass is expressed in pounds, the term pound-mole is used and $2{\cdot}73 \times 10^{26}$ can then be called a pound-mole. If only the term mole is used, it is realised that it means gram-mole.

(iv) Molecular formula of a compound from its volumetric composition. Avogadro's hypothesis, can be applied to determine the molecular formula of gaseous compounds.

Molecular formula of marsh gas. It is found experimentally that 1 volume of marsh gas (methane) contains 2 volumes of hydrogen. Let n be the number of molecules present in 1 volume of marsh gas. Then by Avogadro's hypothesis, n molecules of marsh gas contain 2n molecules of hydrogen or, 1 molecule of marsh gas contains 2 molecules of hydrogen. Now, it has been shown that hydrogen molecule is diatomic, i.e., each molecule contains two atoms. Hence, 1 molecule of marsh gas contains 4 atoms of hydrogen. Therefore, the molecular formula of marsh gas can be written as C_xH_4, where x is the number of carbon atoms present in 1 molecule of marsh gas.

Now, the relative density of marsh gas is determined experimentally to be 8.

$\therefore$ its molecular weight $= 2 \times 8 = 16$

Hence, we get, $x \times 12 + 4 \times 1 = 16$

$\therefore$ $x = 1$ ($\because$ 12=atomic weight of carbon, 1=atomic weight of H)

$\therefore$ The true molecular formula of marsh gas is CH_4.

Molecular formula of steam. It is found experimentally that 2 volumes of hydrogen combine with 1 volume of oxygen to form 2 volumes of steam. Let n be the number of molecules present in 1 volume of oxygen. Then by Avogadro's hypothesis, under the same conditions of temperature and pressure 2 volumes of hydrogen contain 2n molecules of hydrogen and 2 volumes of steam contain 2n molecules of steam. Hence,

2n molecules of hydrogen + n molecules of oxygen = 2n molecules of steam.

$\therefore$ 1 molecule of hydrogen + $\frac{1}{2}$ molecule of oxygen = 1 molecule of steam.

$\therefore$ 2 atoms of hydrogen + 1 atom of oxygen = 1 molecule of steam. [$\because$ hydrogen and oxygen molecules are diatomic.]

Hence, the empirical formula of steam is H_2O and its molecular formula is $(H_2O)_x$ where x is a whole number.

Experimentally, it is found that the vapour density of steam is 9. Hence, its molecular weight is $9 \times 2 = 18$.

$\therefore \quad (2 \times 1 + 16) \times x = 18. \quad \therefore \quad x = 1.$

Hence, the molecular formula of steam is H_2O.

Molecular formula of ammonia. Experimentally, it is found that 1 volume of nitrogen combines with 3 volumes of hydrogen to form 2 volumes of ammonia. Let n be the number of molecules present in 1 volume of nitrogen. By Avogadro's hypothesis, under the same condition of temperature and pressure 3 volumes of hydrogen contain 3n molecules of hydrogen and 2 volumes of ammonia contain 2n molecules of ammonia. Hence,

n molecules of nitrogen + 3n molecules of hydrogen = 2n molecules of ammonia.

$\therefore$ $\frac{1}{2}$ molecule of nitrogen + $\frac{3}{2}$ molecules of hydrogen = 1 molecule of ammonia.

$\therefore$ 1 atom of nitrogen + 3 atoms of hydrogen = 1 molecule of ammonia.

[$\because$ hydrogen and nitrogen molecules are diatomic.]

Hence, 1 molecule of ammonia contains 1 atom of nitrogen and 3 atoms of hydrogen. Hence, the empirical formula of ammonia is NH_3 and its molecular formula is $(NH_3)_x$ where x is a whole number.

Now, vapour density of ammonia is 8·5. Hence, its molecular weight is $8{\cdot}5 \times 2 = 17$. Therefore,

$(14 + 3) \times x = 17. \quad \therefore \quad x = 1.$

$\therefore$ Molecular formula of ammonia is NH_3.

Molecular formula of carbon dioxide. Experimentally, it is found that carbon dioxide contains its own volume of oxygen. In other words, 1 volume of carbon dioxide contains 1 volume of oxygen. Let n be the number of molecules present in 1 volume of carbon dioxide. Then according to Avogadro's hypothesis, under the same conditions of temperature and pressure.

n molecules of carbon dioxide contain n molecules of oxygen.

∴ 1 molecule of carbon dioxide contain 1 molecule of oxygen.

∴ 1 molecule of carbon dioxide contains 2 atoms of oxygen. [∵ oxygen molecule is diatomic.]

Let us suppose that x is the number of carbon atoms present in 1 molecule of carbon dioxide. Then its molecular formula is C_xO_2.

The vapour density of carbon dioxide is 22.

∴ Its molecular weight is $22 \times 2 = 44$.

∴ $x \times 12 + 2 \times 16 = 44$ ∴ $x = 1$.

∴ Molecular formula of carbon dioxide is CO_2.

Molecular formula of nitric oxide. Experimentally, it is found that equal volumes of nitrogen and oxygen combine to form nitric oxide. That is, 1 volume of nitrogen combines with 1 volume of oxygen to form nitric oxide. The vapour density of nitric oxide is 15. Therefore,

1 volume of nitrogen + 1 volume of oxygen→nitric oxide.

Let n be the number of molecules of nitrogen present in 1 volume of nitrogen. Then by Avogadro's hypothesis, at the same temperature and pressure 1 volume of oxygen contains n molecules of oxygen.

∴ n molecules of nitrogen + n molecules of oxygen→nitric oxide.

∴ 1 molecule of nitrogen + 1 molecule of oxygen→nitric oxide.

∴ 2 atoms of nitrogen + 2 atoms of oxygen→nitric oxide. [∵ nitrogen and oxygen molecules are diatomic.]

∴ 1 atom of nitrogen + 1 atom of oxygen→nitric oxide.

∴ The ratio of the number of atoms of oxygen and nitrogen in nitric oxide is 1 : 1.

Hence, the empirical formula of nitric oxide is $(NO)_x$ where x is a whole number.

Now vapour density of nitric oxide is 15.

∴ Its molecular weight is $15 \times 2 = 30$.

∴ $(14 + 16)x = 30$. ∴ $x = 1$.

∴ Molecular formula of nitric oxide is NO.

(v) **Determination of atomic weight.** The Avogadro's hypothesis can be used in the determination of the correct atomic weights of the elements.

(a) **Determination of atomic weight from the atomicity of elementary gases.** Atomic weights of elements which can exist as simple gas molecules are determined from the following relation :

atomic weight = molecular weight ÷ atomicity.

The molecular weight is determined from the relative density from the relation, molecular weight = 2 × relative density. The relative density can be determined experimentally. The relative density of nitrogen, for example, is 14. Hence, its molecular weight is $2 \times 14 = 28$. Now, the atomicity of nitrogen is 2. Hence, atomic weight of nitrogen is 14.

(b) **Determination of the atomic weights of elements that can form a considerable number of gaseous or volatile compounds. Cannizzaro's method.** There are three steps in this method :

(i) Experimental determination of the relative densities of a number of volatile compounds of the element.

(ii) Calculation of their molecular weights from the relation :

Molecular weight = 2 × relative density.

(iii) Direct analysis of the compound to determine the percentage of the element in each of these compounds. The actual weight of the element present in the molecular weight of each compound is then determined. The smallest weight of the element present in the molecular weight is taken as the atomic weight of the element.

The application of this method is illustrated below :

Carbon forms a large number of volatile and gaseous compounds. In the case of carbon monoxide, the calculation may be carried out as follows :

Relative density of carbon monoxide = 14 ; hence its mol. wt. = 28. The percentage of carbon in this molecule = 42·9.

The weight of carbon in the molecular weight of carbon monoxide is, therefore,

$$\frac{42{\cdot}9 \times 28}{100} = 12{\cdot}0.$$

Similar calculations are carried out in a number of gaseous or volatile compounds of carbon and the results are represented in the table 4.2.

Table 4.2

Compound	Relative density D	Molecular weight $M=2\times D$	Percentage of carbon	Weight of carbon in the molecular weight of the compound
Carbon monoxide	14	28	42·9	12·0 $(=12\times 1)$
Carbon dioxide	22	44	27·3	12·0 $(=12\times 1)$
Methane	8	16	74·9	12·0 $(=12\times 1)$
Ethylene	14	28	85·7	24·0 $(=12\times 2)$
Carbon disulphide	38	76	15·76	11·98 $(=12\times 1)$
Chloroform	59·35	118·7	10·4	12·3 $(=12\times 1)$
Ethyl ether	37	74	64·86	48 $(=12\times 4)$
Alcohol	22·8	45·6	52·2	23·8 $(=12\times 2)$
Acetone	29	58	62·07	36·0$(=12\times 3)$
Benzene	38·85	77·7	92·3	71·7 $(=12\times 6)$
Naphthalene	64	128	93·75	120 $(=12\times 10)$

The smallest weight of carbon in the molecular weight of the above compounds is 12. Since this is the smallest weight ever found in any compound of carbon, 12 is assumed to be the atomic weight of carbon.

Table 4.3 : Determination of atomic weight of nitrogen.

Compounds of nitrogen	Vapour density (D)	Molecular weight (M) $M=2\times D$	Percentage of nitrogen	Weight of nitrogen (gram) present in 1 gram-molecule of the compound
Ammonia	8·5	17	82·3	14 $(=14\times 1)$
Nitrous oxide	22	44	63·6	28 $(=14\times 2)$
Nitric oxide	15	30	46·6	14 $(=14\times 1)$
Nirogen dioxide	23	46	30·4	14 $(=14\times 1)$
Dinitrogen tetroxide	46	92	30·4	28 $(=14\times 2)$

The smallest weight of nitrogen in the gram-molecular weight of the above compounds is 14 grams. Hence, the probable atomic weight of nitrogen is 14.

Limitations of Cannizzaro's method. (1) This method is applicable only to those elements which can form a large number of volatile or gaseous compounds. (2) This method is based on the supposition that out of a large number of compounds of an element, at least one compound contains a single atom in its molecules. But this supposition may not be true in all cases. Hence, the atomic weight determined by this method may not be the correct atomic weight.

Importance of Avogadro's hypothesis in Chemistry. Avogadro's hypothesis plays an important role in the advancement of Chemistry. Although the hypothesis has not been proved by direct experiment, the deductions made from it have been found to be in exact agreement with the experimental results. For this reason, it is also called Avogadro's theory.

(1) Avogadro's hypothesis first introduced the concept of molecule and made a clear distinction between atoms and molecules. It modifies the Dalton's atomic theory and establishes it on a firm basis.

(2) It has been possible to determine the atomicity of the molecules of gaseous elements with the help of Avogadro's hypothesis.

(3) Avogadro's hypothesis explains clearly the Gay-Lussac's law of gaseous volumes.

(4) The important deductions which are made from Avogadro's hypothesis are mentioned below :

(i) The molecules of gaseous elements (viz., hydrogen, oxygen, nitrogen, etc.) are diatomic.

(ii) Molecular weight of a substance is twice its vapour density.

(iii) The molar volume of all gaseous substances is the same and is equal to 22·4 litres at N. T. P.

(iv) Molecular formula of a gaseous compound can be determined from its volumetric composition.

(v) This hypothesis helps in the determination of atomic weight of elements (Cannizzaro's method).

All these deductions have been of immense help in the advancement of Chemistry.

Experimental determination of relative densities. The relative density of a volatile liquid can be determined by the following methods :

(i) **Victor Meyer's method.** In this method, a known weight of liquid is vaporised and its vapour is caused to displace its own volume of air, which is collected and measured at the temperature of the room.

The apparatus consists of a long glass tube 'a' with a bulb 'b' at its end. A bent gas delivery tube 'S' leading to a pneumatic trough is fused into the upper part of the long tube 'a'. The tube is then placed into the flask 'c' containing a liquid whose boiling point is about 30° higher than that of the liquid whose relative density is to be determined. A rubber stopper is inserted in the mouth of the tube 'a'. The liquid in the flask 'c' is heated to boiling, the air in the tube 'a' expands and is expelled through the tube 'S' as bubbles. When the stream of air bubbles ceased, indicating that the temperature has become constant, a measuring tube T filled with water is brought over the end of the tube S. A small bottle D is first weighed empty and then weighed again after having been filled with the liquid whose vapour density is to be determined. The rubber stopper is removed and the bottle D is dropped into the tube 'a', the stopper being quickly replaced. A little glass wool or mercury is placed in the bottom of the tube "a" to prevent fracture.

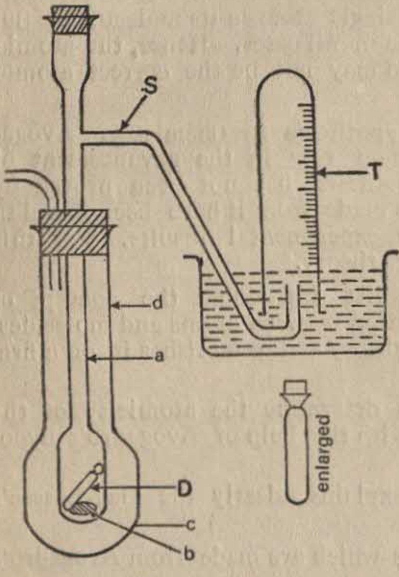

Fig. 4.4

The liquid in D quickly vaporises (the stopper of D is blown out) and the vapour displaces its own volume of air which is collected in the graduated tube. When no further bubbles of air pass into the graduated tube, the water levels in the graduated tube and in the cylinder are equalised and the volume of air is read off and the temperature and barometric pressure are noted.

Calculation. Let the weight of empty bottle $= W_1$ grams
the weight of the bottle + liquid $= W_2$ grams
volume of air displaced $=$ Vc.c.
temperature of water $= t°C$
barometric pressure $=$ P mm. of Hg.
aqueous tension at $t°C = f$ mm. of Hg.

Weight of liquid taken $= (W_2 - W_1)$ grams.

$$\therefore \text{ volume at N. T. P.} = \frac{V(P-f)\times 273}{(273+t)\times 760}\text{ c.c.} = V_1 \text{ c.c. (say)}$$

Now, it is found experimentally that

1000 c.c. of hydrogen weigh 0·09 gram at N.T.P.

$\therefore$ V_1 c.c. of hydrogen weigh $\frac{0{\cdot}09 \times V_1}{1000} = 0{\cdot}00009 \times V_1$ grams at N.T.P.

Hence, the relative density of the liquid $= \frac{(W_2 - W_1)}{0{\cdot}00009 \times V_1}$

$$= \frac{W_2 - W_1}{9V_1} \times 10^{+5}$$

(b) **Measurement of relative densities of gases by diffusion.** The apparatus consists of a glass tube about 70 cms. long and 1 cm. wide. The tube is sealed at one end with a thin plug of plaster of paris which acts as porous diaphragm. There are three rubber bands x, y and z round the tube. The tube is first filled with hydrogen and immersed upto the mark x in a jar of water. As hydrogen diffuses through the porous diaphragm, water rises inside the tube. The time taken, T_{H_2} for water to rise upto the mark y is noted. The experiment is repeated with other gases and the time T_g required for water to rise upto the same mark y is noted. The relative density of the gas is calculated from the following equation (see diffusion).

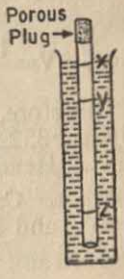

Fig. 4.5

$\frac{\sqrt{D_g}}{\sqrt{D_{H_2}}} = \frac{T_g}{T_{H_2}}$ where D_g = relative density of the gas and D_{H_2} = relative density of hydrogen.

Since the relative density of hydrogen is 1, the relative density of the gas can be calculated from the above equation.

Problems

Ex. 1. Two volumes of nitrogen oxide, NO, unite with one volume of oxygen to produce two volumes of a new gas. Deduce the formula of the new gas.

Solution : By Avogadro's hypothesis, we know that equal volumes of all gases at the same temperature and pressure contain the same number of molecules. Let n be the number of molecules present in 1 volume of oxygen. Now, according to the data presented in the problem, we get,

2 vol. of nitrogen oxide + 1 vol. of oxygen = 2 vols of the new gas.

$2n$ molecules of nitrogen oxide + n molecules of oxygen = $2n$ molecules of the new gas.

2 molecules of nitrogen oxide + 1 molecule of oxygen = 2 molecules of the new gas.

Let N_xO_y be the formula of the new gas. Then the reaction can be expressed by the following equation :

$2NO + 1\ O_2 = 2N_xO_y$ [∵ oxygen molecule is diatomic.] Calculating the number of nitrogen atoms and oxygen atoms in the left hand side of the equation, we get $x=1, y=2$. Hence, the formula of the new gas will be NO_2.

Ex. 2. 111·4 c.c. of a dry gas weighs 0·28522 grams at 27°C and 750 mm. of Hg. Calculate the molecular weight of the gas.

Solution : Let V c.c. be the volume of the gas at N.T.P.

Hence, $\frac{760 \times V}{273} = \frac{111{\cdot}4 \times 750}{300}$

or, $V = \frac{111{\cdot}4 \times 750 \times 273}{760 \times 300} = 100$ c.c.

Therefore, 100 c.c. of the gas weigh 0·28522 grams. Or, 1 litre weighs 2·8522 grams. Therefore, 22·4 litres weigh 22·4 × 2·8522 = 64 grams. Hence, the molecular weight of the gas is 64.

Ex. 3. Calculate the weight of 100 litres of hydrogen chloride at 100°C and 756 mm. pressure.

Solution : Let V be the volume of hydrogen chloride at N.T.P.

Then, $\frac{760 \text{ mm.} \times V}{273 \text{ deg.}} = \frac{100 \text{ litre} \times 756 \text{ mm.}}{373 \text{ deg.}}$

or, $V = \frac{100 \times 756 \times 273}{373 \times 760} = 72{\cdot}8$ litres.

The gram-molecular weight of hydrogen chloride is 36·5 grams and this weight occupies 22·4 litres at N.T.P. Hence, 22·4 litres of hydrogen chloride weigh 36·5 grams. ∴ 72·8 litres of hydrogen chloride weigh $\frac{36{\cdot}5 \times 72{\cdot}8}{22{\cdot}4} = 118{\cdot}59$ grams.

Ex. 4. What is the density of sulphur dioxide at standard conditions ? Vapour density of sulphur dioxide is 32.

Solution : Molecular weight of sulphur dioxide = 2 × 32 = 64. At standard conditions, 64 grams of sulphur dioxide occupy 22·4 litres. The density is weight per unit volume, that is,

Density of sulphur dioxide $= \frac{64}{22{\cdot}4} = 2{\cdot}857$ grams/litre.

Ex. 5. Find the density of chlorine at 27°C. Molecular weight of chlorine is 71.

Solution : The weight of 1 litre of chlorine at standard conditions is $\frac{71g}{22{\cdot}4 \text{ litre}} = 3{\cdot}17$ gram/litre.

Let ρ_2 be the density of the gas at 27°C.
Since the densities vary inversely as the absolute temperature,

$$\frac{3{\cdot}17\text{ g/litre}}{\rho_2}=\frac{(273+27)}{(273+0)}=\frac{300}{273}\quad\text{or,}\quad\frac{\rho_2}{3{\cdot}17\text{ g/litre}}=\frac{273}{300}$$

$$\text{or,}\quad \rho_2=\frac{273}{300}\times 3{\cdot}17\text{ gram/litre.}=2{\cdot}9347\text{ gram/litre.}$$

Hence, the density of chlorine at 27°C=2·9347 gram/litre.

Ex. 6. 0·1298 gram of carbon tetrachloride when vaporised in Victor Meyer's apparatus displaced 20·0 c.c. of air collected over water at 15°C and 769·7 mm. of Hg. Calculate the molecular weight of the substance. Aqueous tension at 15°C=12·7 mm. of Hg.

Solution : Volume of vapour=Volume of air displaced. Volume of air at N.T.P.$=20\times\frac{(769{\cdot}7-12{\cdot}7)}{760}\times\frac{273}{288}=18{\cdot}9$ c.c.

Hence, 0·1298 gram of carbon tetrachloride occupies 18·9 c.c. at N.T.P. Hence, normal density of carbon tetrachloride is

$$\frac{0{\cdot}1298\text{ gram}}{18{\cdot}9\text{ c.c.}}\quad\text{or,}\quad\frac{0{\cdot}1298\text{ gram}}{0{\cdot}0189\text{ litre}}=6{\cdot}87\text{ gram/litre,}$$

Hence, gram-molecular weight=6·87 gram/litre × 22·4 litre
=154 gram

$\therefore$ molecular weight=154.

Ex. 7. What volume will 34 grams of ammonia, NH_3, occupy at 100°C and 400 mm. pressure ?

Solution. Gram-molecular weight of ammonia=(14+3×1)
=17 grams

17 grams of ammonia occupy 22·4 litres at N.T.P.

$\therefore$ 34 grams of ammonia occupy 44·8 litres at N.T.P.

Let V_2 be the volume of the gas at 100°C and 400 mm. pressure.

$$\text{Then,}\ \frac{760\times 44{\cdot}8}{273}=\frac{400\times V_2}{373}$$

$$\therefore\ V_2=\frac{760\times 44{\cdot}8\times 373}{273\times 400}=116{\cdot}27\text{ litres.}$$

Ex. 8. 111·4 c.c. of a diatomic gas weighs 0·28522 grams at 27°C and 750 mm of Hg. Calculate the atomic weight of the gas. Also calculate the weight in gram of one atom.

Solution. Let Vc.c. be the volume of the gas at N. T. P.

$$\text{Hence,}\quad\frac{760\times V}{273}=\frac{111{\cdot}4\times 750}{300}$$

$$\text{or,}\ V=\frac{111{\cdot}4\times 750\times 273}{760\times 300}=100\text{ c.c.}$$

Therefore, 100 c.c. of the gas weigh 0·28522 grams or, 1 litre weighs 2·8522 grams. Therefore, 22·4 litre weigh 22·4 × 2·8522 = 64 grams. Hence, the molecular weight of the gas is 64.

$$\text{Its atomic weight} = \frac{64}{2} = 32$$

$$\therefore \text{ Weight of one atom} = \frac{32 \text{ gram}}{6{\cdot}023 \times 10^{23}} = 5{\cdot}311 \times 10^{-23} \text{ gram.}$$

Ex. 9. A gas mixture containing 80% CO and 20% CO_2 by volume exists at 27°C and 750 mm pressure. How many grams of CO_2 are present in 1·52 litres of this gas mixture ? [H. S., '78]

Solution. Let the volume of the gas mixture at N. T. P. be V_2.

$$\text{Then, } \frac{750 \text{ mm} \times 1{\cdot}52 \text{ litres}}{300} = \frac{760 \text{ mm} \times V_2}{273}$$

$$\therefore V_2 = \frac{750 \times 1{\cdot}52 \times 273}{760 \times 300} = 1{\cdot}364 \text{ litres.}$$

$$\therefore \text{ Volume of } CO_2 \text{ at N. T. P.} = \frac{20 \times 1{\cdot}364}{100} = 0{\cdot}2728 \text{ litres.}$$

Mol. wt. of $CO_2 = (12 + 2 \times 16) = 44$

Now, 22·4 litres of CO_2 at N. T. P. weigh 44 grams

$$\therefore 0{\cdot}2728 \text{ litres of } CO_2 \text{ at N. T. P. weigh } \frac{44 \times 0{\cdot}2728}{22{\cdot}4} = 0{\cdot}536 \text{ grams.}$$

Hence, 0·536 gram of CO_2 is present in 1·52 litre of the gas mixture.

Ex. 10. 250 c.c. of a gas at N. T. P. weigh 0·7317 gram. The density of hydrogen at N. T. P. is 0·08987 gram/litre. What is the vapour density of the gas ? Calculate its molecular weight. [J. E. E., '78]

Solution. Weight of 1 litre of the gas at N. T. P.

$$= \frac{0{\cdot}7317 \times 1000}{250} = 2{\cdot}9268 \text{ gram}$$

Weight of 1 litre of hydrogen at N. T. P. = 0·08987 gram.

Vapour density of the gas

$$= \frac{\text{Weight of 1 litre of the gas at N. T. P.}}{\text{Weight of 1 litre of hydrogen at N. T. P.}}$$

$$= \frac{2{\cdot}9268}{0{\cdot}08987} = 32{\cdot}567.$$

$$\therefore \text{ Molecular weight of the gas} = 32{\cdot}567 \times 2 = 65{\cdot}134.$$

Ex. 11. From 200 mg of CO_2, 10^{21} molecules are removed. How many moles of CO_2 are left ? [I. I. T., '78]

Solution. Gram-molecular weight of CO_2

$$=(12+2\times 16) \text{ gram}=44 \text{ gram}$$

Hence, 44×1000 mg is the weight of 1 mole of CO_2

$\therefore$ 200 mg. is the weight of $\dfrac{1\times 200}{44\times 1000}=0{\cdot}004545$ mole of CO_2

$6{\cdot}023\times 10^{23}$ molecules are present in 1 mole of CO_2.

$\therefore$ 10^{21} molecules are present in $\dfrac{1\times 10^{21}}{6{\cdot}023\times 10^{23}}=0{\cdot}00166$ mole of CO_2.

Hence, mole of CO_2 left$=0{\cdot}004545-0{\cdot}001660$

$$=0{\cdot}002885.$$

Ex. 12. Assuming the density of water to be 1 gram/c.c., find the volume occupied by one molecule of water. The atom of oxygen in this molecule occupies about half of the above volume. What is the approximate diameter of an oxygen atom ? [I. I. T., '69]

Solution : Gram-molecular weight of water$=18$ grams

Volume of 18 grams of water$=18$ c.c.

18 grams of water contain $6{\cdot}023\times 10^{23}$ water molecules.

$\therefore$ 18 c.c. of water contain $6{\cdot}023\times 10^{23}$ water molecules.

Hence, volume of $6{\cdot}023\times 10^{23}$ water molecules$=18$ c.c.

$$\therefore \text{ Volume of 1 water molecule}=\frac{18}{6{\cdot}023\times 10^{23}}$$

$$=2{\cdot}988\times 10^{-23} \text{ c.c.}$$

$$\text{Now, volume of 1 atom of oxygen}=\frac{2{\cdot}988\times 10^{-23}}{2}$$

$$=1{\cdot}494\times 10^{-23} \text{ c.c.}$$

Let the radius of the oxygen atom be r, then $\frac{4}{3}\pi r^3=1{\cdot}494\times 10^{-23}$.

or, $\frac{4}{3}\times\frac{22}{7}\times r^3=1{\cdot}494\times 10^{-23}$

$$\therefore\quad r=\left(\frac{1{\cdot}494\times 10^{-23}\times 7\times 3}{4\times 22}\right)^{\frac{1}{3}}$$

$$=(3{\cdot}565\times 10^{-24})^{\frac{1}{3}}=1{\cdot}5276\times 10^{-8} \text{ cm.}$$

$\therefore$ Diameter of oxygen molecule$=2\times 1{\cdot}5276\times 10^{-8}$ cm.

$$=3{\cdot}0552\times 10^{-8} \text{ cm.}$$

Ex. 13. 33·6 c.c. of phosphorus vapour weigh 0·0625 gram at 546°C and 76 cm. Hg pressure. What is the molecular weight of phosphorus ? How many atoms are there in one molecule of phosphorus vapour ? [I. I. T., '69]

Solution : Let the volume of phosphorus vapour at N.T.P. be V_1 c.c.

Hence, $\frac{V_1 \times 76}{273} = \frac{33{\cdot}6 \times 76}{(546+273)}$, whence $V_1 = 11{\cdot}07$ c.c.

$\therefore$ 11·07 c.c. of the vapour at N.T.P. weigh 0·0625 gram

$\therefore$ 22400 c.c. of the vapour at N.T.P. weigh $\frac{0{\cdot}0625 \times 22400}{11{\cdot}07}$ gram

$= 126{\cdot}34$ grams.

$\therefore$ Molecular weight of phosphorus $= 126{\cdot}34$

Atomic weight of phosphorus $= 31$

$\therefore$ Number of atoms in 1 molecule of phosphorus vapour

$= \frac{126{\cdot}34}{31} = 4.$

Ex. 14. In an experiment, radium disintegrates giving $1{\cdot}602 \times 10^{17}$ alpha particles (i.e., $1{\cdot}602 \times 10^{17}$ helium atoms). The resultant helium gas occupied 0·5 c.c. at 27°C and 10 mm. pressure. Calculate the Avogadro number.

Solution : Let *n* be the number of moles of helium present in helium gas. Then, $n = \frac{PV}{RT} = \frac{10/760 \text{ atm} \times 0{\cdot}5 \times 10^{-3} \text{ litre}}{0{\cdot}082 \text{ litre-atm/deg. K. mole} \times 300^\circ\text{K}}$

$= 0{\cdot}266 \times 10^{-6}$ mole

Hence, $0{\cdot}266 \times 10^{-6}$ mole of helium contain $1{\cdot}602 \times 10^{17}$ helium atoms.

$\therefore$ 1 mole of helium contain $\frac{1{\cdot}602 \times 10^{17}}{0{\cdot}266 \times 10^{-6}} = 6{\cdot}02 \times 10^{23}$

$\therefore$ Avogadro number calculated in this way is $6{\cdot}02 \times 10^{23}$.

Ex. 15. A molecule of a compound contains 4 hydrogen atoms, 1 oxygen atom, 2 nitrogen atom and 2×10^{-23} gram of another element. Calculate the molecular weight of the compound.

$[N = 6 \times 10^{23}]$

Solution : The weight of 6×10^{23} hydrogen atoms $= 1$ gram

$\therefore$ The weight of 4 hydrogen atoms $= \frac{1 \times 4}{6 \times 10^{23}}$ gram

$= 0{\cdot}666 \times 10^{-23}$ gram.

The weight of 1 atom of oxygen $= \frac{16}{6 \times 10^{23}} = 2{\cdot}666 \times 10^{-23}$ gram.

The weight of 2 atoms of nitrogen $= \frac{14 \times 2}{6 \times 10^{23}}$ gram

$= 4{\cdot}666 \times 10^{-23}$ gram.

$\therefore$ Total weight$=(0{\cdot}666\times10^{-23}+2{\cdot}666\times10^{-23}+4{\cdot}666\times10^{-23}$
$+2\times10^{-23})$ gram

$=9{\cdot}998\times10^{-23}$ gram.

1 atomic mass unit$=1{\cdot}66\times10^{-24}$ gram

$\therefore$ Molecular weight$=\dfrac{9{\cdot}998\times10^{-23}}{1{\cdot}66\times10^{-24}}=60{\cdot}2.$

Ex. 16. The weight of 1 atom of an element X is $6{\cdot}644\times10^{-23}$ gram. How many gram-atoms of the element are present in 40 kilograms of the element ? [I. I. T., '75.]

Solution : 1 gram-atom of the element, X, contains $6{\cdot}02\times10^{23}$ atoms.

The weight of 1 atom of X$=6{\cdot}644\times10\ ^{23}$ gram

$\therefore$ The weight of $6{\cdot}02\times10^{23}$ atoms of X$=6{\cdot}644\times10^{-23}$
$\times6{\cdot}02\times10^{23}$ gram
$=40$ gram.

Now, 40 gram$=$1 gram-atom of the element

$\therefore$ 40×1000 gram$=$1000 gram-atoms of the element

$\therefore$ 40 kilograms of the element contain 1000 gram-atoms of the element.

Ex. 17. The atomic weight of germanium (Ge) is $72{\cdot}6$ and its density is $5{\cdot}4$ gram/c.c. What is the volume of 1 atom of germanium ? What is the radius of its atom ?

Solution : 1 gram-atom of Ge$=72{\cdot}6$ gram

$\therefore$ The volume of 1 gram-atom$=\dfrac{72{\cdot}6}{5{\cdot}4}=13{\cdot}44$ c.c.

Again, 1 gram-atom of Ge contains $6{\cdot}02\times10^{23}$ atoms.

$\therefore$ The volume of $6{\cdot}02\times10^{23}$ atoms$=13{\cdot}44$ c.c.

$\therefore$ The volume of 1 atom$=\dfrac{13{\cdot}44}{6{\cdot}02\times10^{23}}=2{\cdot}23\times10^{-23}$ c.c.

Let *r* be the radius of germanium atom. Then,

$\frac{4}{3}\pi r^3=2{\cdot}23\times10^{-23}$

$\therefore$ $\frac{4}{3}\times\frac{22}{7}\times r^3=2{\cdot}23\times10^{-23}$

$\therefore$ $r^3=5{\cdot}32\times10^{-24}$ cm.

$\therefore$ $r=1{\cdot}7457\times10^{-8}$ cm.

Ex. 18. What is the weight of $111{\cdot}4$ c.c. of a gas at 27°C and 750 mm. pressure ? Vapour density of the gas is 32.

Solution : Let V c.c. be the volume of the gas at N.T.P. Then

$$\frac{760\times V}{273}=\frac{111{\cdot}4\times750}{300}\quad\therefore\quad V=100\text{ c.c.}$$

The vapour density of the gas $= 32$

$\therefore$ Its molecular weight $= 32 \times 2 = 64$

Now, weight of 22400 c.c. of the gas at N.T.P. $= 64$ grams

$\therefore$ The weight of 100 c.c. of the gas at N.T.P.

$$= \frac{64 \times 100}{22400} = 0{\cdot}285 \text{ gram.}$$

$\therefore$ The weight of 111·4 c.c. of the gas at 27°C and 750 mm. pressure is 0·285 gram.

Ex. **19.** At the same condition of temperature and pressure, the density of a gaseous element is 5 times the density of oxygen. If the molecule of the element is triatomic, what is the atomic weight of the element? **[H. S., '80]**

Solution : The relative density of oxygen $(H = 1) = 16$

$\therefore$ The relative density of the gas $= 16 \times 5 = 80$

$\therefore$ The molecular weight of the gaseous element $= 2 \times 80 = 160$

$$\text{Now, atomic weight of the element} = \frac{\text{Molecular weight}}{\text{Atomicity}}$$

$$= \frac{160}{3} = 53{\cdot}33.$$

Ex. **20.** An element E forms two gaseous hydrides A and B. The compound A and B contains 75% and 80% E respectively. The vapour densities of the two compounds are 8 and 15 respectively. If the molecule of A contains one atom of E, what is the atomic weight of E. Determine the formula of A and B. **[H. S., '64]**

Solution : The molecular weight of $A = 8 \times 2 = 16$

The molecular weight of $B = 15 \times 2 = 30$

Let the molecular formula of A be EH_n

$$\therefore \frac{\text{The number of atoms of E}}{\text{The number of atoms of H}} = \frac{\frac{75}{a}}{\frac{25}{1}} = \frac{1}{n}$$

[a = atomic weight of E]

$$\therefore \frac{75}{a} \times \frac{1}{25} = \frac{1}{n} \quad \therefore 75n = 25a$$

$$\therefore a = \frac{75n}{25} = 3n \qquad (1)$$

Again, $a + n \times 1 = 16$

$\therefore 3n + n = 16 \qquad \therefore n = 4$

$\therefore a = 4 \times 3 = 12$

$\therefore$ Atomic weight of E $= 12$

The formula of A is EH_4.

Let the molecular fomula of B be E_pH_q

$$\therefore \quad p\times 12+q\times 1=30 \qquad \dots (2)$$

Again, $\frac{80/12}{20/1}=\frac{p}{q}$ or, $\frac{p}{q}=\frac{1}{3}$

$$\therefore \quad 3p=q \qquad \dots (3)$$

From equations (2) and (3) we get

$$12p+3p=30 \quad \therefore \; 15p=30 \quad \therefore \; p=2$$

$$\therefore \quad q=6$$

Hence, the molecular formula of B is E_2H_6.

Ex. 21. From the following data, calculate the atomic weight of oxygen by Cannizzaro's method :

Compounds	Vapour density (H = 1)	% Oxygen
Water vapour	9	88·9
Carbon dioxide	22	72·9
Sulphur dioxide	32	50
Nitric oxide	15	53·33

Solution. **Water vapour** : Molecular weight $=9\times 2=18$

Amount of oxygen present in 1 gram-molecule of

$$\text{water vapour}=\frac{88{\cdot}9\times 18}{100}=16$$

Carbon dioxide : Molecular weight $=22\times 2=44$

Amount of oxygen present in 1 gram-molecule of

$$\text{carbon dioxide}=\frac{72{\cdot}9\times 44}{100}=32$$

Sulphur dioxide : Molecular weight $=32\times 2=64$

$\therefore$ Amount of oxygen present in 1 gram-molecular

$$\text{weight of sulphur dioxide}=\frac{50\times 64}{100}=32$$

Nitric oxide : Molecular weight $=15\times 2=30$

$\therefore$ Amount of oxygen present in 1 gram-molecular

$$\text{weight of nitric oxide}=\frac{53{\cdot}33\times 30}{100}=16$$

The results are tabulated below :

Compound	Vapour density (H=1)	Molecular weight (M=2D)	% Oxygen	Amount of oxygen present in 1 gram-molecular weight of the compound
Water vapour	9	18	88·9	16 (=16×1)
Carbon dioxide	22	44	72·9	32 (=16×2)
Sulphur dioxide	32	64	50	32 (=16×2)
Nitric oxide	15	30	53·33	16 (=16×1)

From these results we find that the minimum amount of oxygen present in one gram-molecular weight of different compounds is 16. Hence, the atomic weight of oxygen is 16.

EXERCISE

I

1. State Gay-Lussac's law of combining volumes. Explain how this law suggests that the particles present in elemental gases may not be atomic particles.

2. State Avogadro's hypothesis. How does this hypothesis explain Gay-Lussac's law of combining volumes ?

3. How will you prove that oxygen cannot be a monatomic molecule ?

4 Enunciate Avogadro's hypothesis. Discuss how this hypothesis has proved useful in the determination of atomic and molecular weight of gases.

5. How will you prove that (a) a molecule of hydrogen contains two atoms (b) the molecular weight is twice the vapour density.

6. What do you understand by a 'mole' and 'molar volume'. Prove that molar volume (or gram-molecular volume) of any gas is 22·4 litres at N.T.P.

7. Distinguish among molecular weight, gram-molecular weight, gram-molecular volume, and Avogadro number. Show how Avogadro's hypothesis leads to the deduction that gram-molecular weight of any gas occupies 22·4 litres at N.T.P.

8. Explain the principle involved in the determination of atomic weight by Cannizzaro's method.

9. Explain what is meant by (a) relative density and (b) normal density. Describe a method for the determination of relative density of a volatile liquid. Hence, calculate the molecular weight of the liquid.

10. Describe an experimentation in which the phenomenon of diffusion is utilised in the determination of the relative density of an elemental gas.

11. Define molecular weight and vapour density. Prove that molecular weight is twice the vapour density. [J. E. E., '69]

12. Prove that the molar volume of all gases is the same and is equal to 22·4 litres at N.T.P.

13. State Avogadro's hypothesis. How does it explain the Gay-Lussac's law of combining volumes? [J.E.E., '73]

14. State the hypothesis which connects the Gay-Lussac's law of combining volumes and Dalton's atomic theory. With the help of this hypothesis, show that molar volume of any gas is 22·4 litres at N.T.P. [J.E.E., '70]

15. With the help of Avogadro's hypothesis, show that the molecular weight of a gas is twice its vapour density. [H. S., '80]

16. (a) State Avogadro's hypothesis. [H. S., '78, '80]

(b) How does this hypothesis explain the Gay-Lussac's law of gaseous volumes?

17. How is the atomic weight of an element determined by Cannizzaro's method with the help of Avogadro's hypothesis? What are the limitations of the method? Give the definition of atomic weight on the basis of the principle of this method.

18. (a) Establish a relation between normal density and vapour density.

(b) How is Dalton's atomic theory modified by Avogadro's hypothesis? What is the usefulness of Avogadro's hypothesis? Mention the role of Avogadro's hypothesis in the advancement of Chemistry.

19. "Under the same conditions of temperature and pressure, equal volumes of all gases contain equal number of atoms."—How and by whom is this hypothesis modified? State the modified hypothesis. With the help of this hypothesis, show that hydrogen molecule is diatomic.

20. Write notes on: (a) Atom and molecule, (b) Mole and Avogadro number.

21. What do you mean by atomicity of elementary gases? How is the atomic weight determined from atomicity of the elementary gases? Explain with an example.

II

22. (i) How is the weight of one atom of an element or the weight of one molecule of a substance determined by Avogadro's hypothesis?

(ii) What is the value of 1 amu in gram?

(iii) What do you mean by 1 mole of oxygen atoms, 1 mole of oxygen molecules and 1 mole of electrons?

(iv) Which of the following contains largest number of molecules?
2 mole of CO_2; 44 grams of CO_2 and 30 litres of CO_2 at N.T.P.

(v) What is the weight of Avogadro number of molecules of oxygen?

(vi) Which of the following contains largest number of atoms?

0·1 gram-atom of nitrogen, 10 grams of nitrogen, 1 mole of nitrogen atoms and 11·2 litres of nitrogen at N.T.P.

(vii) Which of the following contains greater number of atoms?
11 grams of sodium and 1 mole of sodium.

(viii) Which one of the following has smaller mass?
2×10^{-20} molecules of oxygen and 0·2 mole of oxygen molecules.

(ix) What is the volume of 32 grams of oxygen at N.T.P.?

(x) You are given 1 gram and 1 gram-atom of an element. Which one will contain greater number of atoms?

(xi) Which one of the following has greater mass?
1 mole of Cl_2, 1 mole of Cl and 1 mole of N_2

23. Applying Avogrado's hypothesis calculate the molecular formula of the compounds from the following results:

(i) 1 volume of nitrogen combines with 3 volumes of hydrogen to form 2 volumes of ammonia. The vapour density of ammonia = 8·5.

(ii) 1 volume of hydrogen combines with 1 volume of chlorine to form 2 volumes of hydrogen chloride. The vapour density of hydrogen chloride is 18·25. [H. S., '60]

(iii) Carbon dioxide contains its own volume of oxygen ; its vapour density is 22. [H. S. (Comp.), '63]

(iv) 2 volumes of hydrogen combine with 1 volume of oxygen to form 2 volumes of steam. The vapour density of steam is 9.

(v) Carbon monoxide contains its half of its volume of oxygen. Its vapour density is 14. [H. S., '64]

III

24. One volume of carbon monoxide unites with one volume of chlorine to produce one volume of phosgene. Determine the formula of phosgene.
[Ans. $COCl_2$]

25. How many molecules does 1 ml. of hydrogen contain at N.T.P. ?
[Ans. $2·6888 \times 10^{19}$ molecules]

26. What is the volume which $2·6888 \times 10^{20}$ molecules would occupy at N.T.P. ? [Ans. 10 c.c.]

27. 1 litre of a gas weighs 1·429 grams at S.T.P. What is (a) the molecular weight of the gas, (b) the gram-molecular weight and (c) the weight of one mole.
[Ans. (a) 32, (b) 32 grams and (c) 32 grams]

28. Calculate the molecular weight of a gaseous compound of which 0·1353 gram occupies 150 ml at 127°C and 750 mm. pressure. [Ans. 30]

29. What volume will 170 grams of ammonia, NH_3, occupy at 227°C and 200 mm. pressure ? N = 14 [Ans. 1557 c.c.]

30. What is the density of carbon dioxide, CO_2, at standard conditions ?
[Ans. 1·96 grams/litre]

31. Calculate the weight of 10 litres of hydrogen sulphide, H_2S, measured at 147°C and 740 mm pressure. The molecular weight of hydrogen sulphide is 34.
[Ans. 9·61 grams]

32. Two volumes of phosphine contain three volumes of hydrogen. If the relative density of phosphine is 17, calculate the true formula of phosphine (At. wt. of P = 31) [Ans. PH_3]

33. Determine the atomic weight of nitrogen by Cannizzaro's method of least weight from the following data :

Compound	Relative density	% Nitrogen
Ammonia	8·5	82·3
Nitrous oxide	22	63·6
Nitric oxide	15	46·6
Dinitrogen tetroxide	46	30·4

[Ans. 14·00]

34. The weight of 350 ml. of a diatomic gas at 0°C and 2 atm pressure is 1 gram. Calculate the weight in gram of one atom.
[Ans. $2·6564 \times 10^{-23}$ gram] [I. I. T., '70]

35. 0·44 gram of a colourless oxide of nitrogen occupies 224 ml. at 1520 mm. Hg and 273°C. Identify the compound. How much in gram does one molecule of this compound weigh ? [Ans. $7{\cdot}305 \times 10^{-23}$ gram] [I. I. T., '71]

[Hints : Determine the molecular weight of the compound. It is 44. Hence the compound is N_2O because its molecular weight is $2 \times 14 + 16 = 44$.]

36. It was found that 380 ml. of a gas at 27°C and 800 mm. of Hg weighed 0·455 gram. Find the molecular weight of the gas. [Ans. 28] [I. I. T., '75]

37. How many molecules of oxygen are present in 1 c.c. of oxygen at N.T.P. ? What is the weight of 1 atom of oxygen ?
[Ans. $2{\cdot}68 \times 10^{19}$ molecules ; $2{\cdot}656 \times 10^{-23}$ gram] [J. E. E., '76]

38. 20·95 litres of nitrous oxide weigh 3·95 gram at 17°C and 770 mm. of Hg. What is the weight of 500 c.c. of the gas at N.T.P. ?
[Ans. 0·197 gram] [J. E. E., '71]

39. The density of a gas is 2·8 gram/litre at 27°C and 740 mm. of Hg. Determine the molecular weight of the gas. [Ans. 70·8]

40. 10 gram of a liquid when vapourised occupy 3·86 litres at N.T.P. Calculate its molecular weight. [Ans. 58·3]

41. What is the density of helium at 527°C and 1520 mm. of Hg ?
[Ans. 0·122 gram/litre]

42. At 4°C the density of water is 1 gram/c.c. If 1 c.c. of water contains 20 drops, calculate the number of molecules present in 1 drop of water.
[Ans. $1{\cdot}67 \times 10^{22}$]

43. On analysis of a carbon compound it is found that it contains 0·6% carbon. If each molecule of the compound cantains 1 carbon atom, what is the molecular weight of the compound ? [Ans. 2000]

44. (a) One atom of an element weighs $2{\cdot}656 \times 10^{-23}$ gram. What is the atomic weight of the element ? [Ans. 16]

(b) One atom of an element weighs $2{\cdot}656 \times 10^{-23}$ gram. Calculate the number of gram-atoms present in 16 kilograms of the element. [Ans. 1000]

45. One molecule of an element weighs $2{\cdot}991 \times 10^{-23}$ gram. What is the molecular weight of the element ? [Ans. 18·016]

46. 2×10^{22} atoms of carbon are removed from 0·6 gram of carbon. What is the number of atoms left ? [Ans. $1{\cdot}0115 \times 10^{22}$]

47. The atomic weight of a metal is 23, and its density is 1 gram/c.c. (i) What is the volume of 1 atom of the metal ? (ii) If the molecule is spherical, what is its radius ? [Ans. $2{\cdot}088 \times 10^{-8}$ cm.]

48. Each molecule of a compound contains 12 carbon atoms, 22 hydrogen atoms and $29{\cdot}216 \times 10^{-23}$ gram of another element. Calculate the molecular weight of the compound. ($N = 6 \times 10^{23}$) [Ans. 341·298]

49. An element E forms two gaseous hydrides A and B. A and B contains 75 and 81·81% of E respectively and their vapour densities are 8 and 22 respectively. If the molecule of A contains 1 atom of E, calculate the atomic weight of E and determine the formula of A and B. [Ans. 12, EH_4 and E_3H_8]

50. Calculate the amount of sulphur which contains twice the number of atoms as is present in 2·4 grams of carbon. [Ans. 12·8 grams]

51. Equal weights of two gases are kept in two separate containers at the same temperature and pressure. If the ratio of the molecular weights of A and B is 2 : 3, what is the ratio of the volumes of the containers. [Ans. 3 : 2] [H.S., '82]

52. One gram of a gas occupies 280 ml. at N.T.P. Calculate the molecular weight of the gas. [Ans. 80]

53. 1·5276 gram of $CdCl_2$ contain 0·9367 gram of cadmium. Calculate the atomic weight of cadmium. ($Cl = 35{\cdot}5$) [Ans. 112·52] [I. I. T., '75]

CHAPTER V

CHEMICAL CALCULATIONS

The derivation of the formula of a compound from its percentage composition.

To establish the formula of a compound, one must require the following four sets of data which are usually found by experiment: (*a*) the elements present (*b*) the percentage of each element which is the weight of each element in 100 parts by weight of the compound (*c*) the gram-molecular weight of the compound and (*d*) the atomic weight of each element present. The first three sets of data are obtained by laboratory work—the first is found by the processes of qualitative analysis, the second by means of a quantitative analysis and the third by the actual measurement of the gram-molecular weight. The atomic weights are obtained from the atomic-weight table.

Let the elements A and B form the compound of formula A_nB_m where n and m are the number of atoms of A and B respectively and let the atomic weights of A and B be a and b respectively. Then the total weight of the elements in the formula is $n \times a + m \times b$. Hence,

$$\text{the percentage of A} = \frac{na \times 100}{na+mb}$$

$$\text{the percentage of B} = \frac{mb \times 100}{na+mb}$$

$$\therefore \quad \frac{\text{the percentage of A}}{\text{the percentage of B}} = \frac{na \times 100}{na+mb} \times \frac{na+mb}{mb \times 100} = \frac{na}{mb}$$

$$\therefore \quad \frac{\text{the percentage of A}}{a} : \frac{\text{the percentage of B}}{b} = n : m$$

$$i.e., \quad \frac{\text{the percentage of A}}{\text{atomic weight of A}} : \frac{\text{the percentage of B}}{\text{atomic weight of B}}$$

$$= \text{the number of atoms of A} : \text{the number of atoms of B}.$$

Hence, the ratio of the numbers of atoms present ($n : m$) is obtained by dividing each percentage by the corresponding atomic weight.

Hence, to calculate the formula from percentage composition :

(i) divide each percentage by the corresponding atomic weight of the element to obtain the ratio of the number of atoms present.

(ii) reduce the ratio of numbers so obtained to a ratio of smallest whole numbers because the number of atoms in a formula must be integral. This may be done by dividing each number by the smallest of them and the ratio of the smallest whole numbers would then be apparent.

The simplest formula or the "least common denominator" formula thus obtained from the percentage composition is known as the *empiricical formula*. Empirical formula is not necessarily the molecular formula. The molecular formula may be the empirical formula or a multiple of empirical formula. Let the empirical formula of a compound be A_rB_s ; $r : s$ being the ratio of simplest whole numbers ; then

$(A_rB_s)_n$ = molecular formula ; where n is a simple integer or $(ra+sb)n$ = molecular weight, where a and b are the atomic weights of A and B respectively.

$$\therefore\ n=\frac{\text{molecular weight}}{ra+sb}$$

The value of n can be determined, provided the molecular weight is known.

For example, in benzene the ratio of its constituent elements C : H = 1 : 1. Hence, its empirical formula is CH. Therefore, its molecular formula is $(CH)_n$. Now the molecular weight of benzene is 78.

$$\therefore\ n=\frac{78}{12+1}=\frac{78}{13}=6$$

$\therefore$ Molecular formula of benzene is C_6H_6.

Glucose contains carbon, hydrogen and oxygen and the ratio of atoms of these elements (C : H : O) = 1 : 2 : 1. Hence, the empirical formula of glucose is $C_1H_2O_1$. It has been found experimentally that the molecular weight of glucose is 180. Hence,

$$\therefore\ n=\frac{180}{12+2+16}=\frac{180}{30}=6$$

$\therefore$ Molecular formula of glucose is $(C_1H_2O_1)\times 6$ or, $C_6H_{12}O_6$.

The calculation of percentage composition from the formula. The percentage composition of a compound expresses the weight of each constituent in 100 parts by weight of the compound. Hence, if the formula of a compound is known, the percentage of each element in the compound can be calculated easily. The weight of each element divided by the molecular weight calculated from the molecular formula times 100 will yield percentage of the element. Thus, to determine the percentage composition of a compound :

(i) Calculate the molecular weight (i.e., the sum of the atomic weight of all the constituent atoms) of the compound from the molecular formula.

(ii) Divide the total weight of the element in the molecular formula by the molecular weight and then multiply the ratio by 100.

Formula weight is used in place of molecular weight when the actual molecular weight has not been determined. The formula weight like the molecular weight of a compound is the sum of the atomic weights of the elements represented by the known or assumed formula of the compound. To illustrate the procedure, let us calculate the percentage of carbon in the compound whose molecular formula is C_2H_6. The molecular weight of the compound is $2 \times 12 + 6 \times 1$ or 30 where 12 is the atomic weight of carbon and 1 is the atomic weight of hydrogen. Hence, 30 parts by weight of C_2H_6 contain 2×12 or 24 parts by weight of carbon.

$\therefore$ 100 parts by weight of C_2H_6 contain $\frac{24 \times 100}{30} = 80{\cdot}0$ parts by weight of carbon.

$\therefore$ percentage of carbon in C_2H_6 is 80·0.

Problems

Ex. 1. A compound is found by chemical analysis to contain 40·00% carbon, 6·72% hydrogen and 53·28% oxygen. The molecular weight of the compound is 60. Calculate the molecular fomula of the compound.

Solution. Dividing the percentage of each element by its atomic weight, we get

$$C = \frac{40{\cdot}00}{12} = 3{\cdot}333\,; \quad H = \frac{6{\cdot}72}{1} = 6{\cdot}72\,; \quad O = \frac{53{\cdot}28}{16} = 3{\cdot}33.$$

The numbers 3·333, 6·72 and 3·33 are approximately in the ratio of the number of atoms present. Dividing the numbers by the lowest number 3·33 to transform them into simple whole numbers, since fractions of atoms are never found in chemical compound, we get

$$C = \frac{3{\cdot}333}{3{\cdot}33} = 1\,; \quad H = \frac{6{\cdot}72}{3{\cdot}33} = 2\,; \quad O = \frac{3{\cdot}33}{3{\cdot}33} = 1.$$

Hence, the simplest or empirical formula of the compound is CH_2O. Its molecular formula is, therefore, $(CH_2O)_n$ where n is a simple integer.

$\therefore$ molecular weight of $(CH_2O)_n = 60$

or, $(12 + 2 \times 1 + 16) \times n = 60 \quad \therefore\ n = \frac{60}{30} = 2.$

$\therefore$ the molecular formula of the compound is $C_2H_4O_2$.

Ex. 2. An analysis of a compound shows that it contains 92·31 per cent carbon and 7·69 per cent hydrogen. The density of the vapour of the compound with respect to hydrogen is 39. What is the molecular formula of the compound ?

Solution. Dividing the percentage by the atomic weight of the respective element, we obtain

$$C=\frac{92{\cdot}31}{12}=7{\cdot}69\ ;\quad H=\frac{7{\cdot}69}{1}=7{\cdot}69$$

Dividing each number by the highest common divisor, we get

$$C=\frac{7{\cdot}69}{7{\cdot}69}=1\ ;\quad H=\frac{7{\cdot}69}{7{\cdot}69}=1$$

Hence, the empirical formula is CH and its molecular formula is $(CH)_n$ where n is an integer. Since the vapour density of the compound is 39, its molecular weight is 78. Therefore, we can write the equation.

$$\text{molecular weight of } (CH)_n=78$$

$$\therefore\ (1\times12+1\times1)\times n=78 \qquad \therefore\ n=6.$$

The molecular formula of the compound is $(CH)_6$ or, C_6H_6.

Ex. 3. Chemical analysis of a compound shows that it contains 37·8% of carbon ; 6·3% of hydrogen and 55·9% of chlorine. When vaporised, 2·59 grams of the compound occupy 624 ml. at 100°C and 775 mm. pressure. What is the molecular formula of the compound ? What is the accurate molecular weight of the compound ?

Solution. Dividing the percentage of each element by its atomic weight, we obtain

$$C=\frac{37{\cdot}8}{12}=3{\cdot}15\ ;\quad H=\frac{6{\cdot}3}{1}=6{\cdot}3\quad Cl=\frac{55{\cdot}9}{35{\cdot}5}=1{\cdot}575.$$

Dividing the numbers thus obtained by their highest common divisor, we get

$$C=\frac{3{\cdot}15}{1{\cdot}575}=2\ ;\quad H=\frac{6{\cdot}3}{1{\cdot}575}=4\quad Cl=\frac{1{\cdot}575}{1{\cdot}575}=1.$$

Hence, the empirical formula is C_2H_4Cl and its molecular formula is $(C_2H_4Cl)_n$ where n is a whole number. Now, let V ml. be the volume occupied by 2·59 grams of the compound at N.T.P.

$$\text{Then,}\quad \frac{V\times760}{273}=\frac{624\times775}{373}$$

$$\therefore\quad V=\frac{624\times273\times775}{760\times373}=466\text{ ml. or, }0{\cdot}466\text{ litre.}$$

The gram-molecular weight is the weight of 22·4 litre at **N.T.P.** Now, 0·466 litre of the compound weighs 2·59 grams at N.T.P.

$\therefore$ 22·4 litres of the compound weigh $\frac{2·59 \text{ gram} \times 22·4 \text{ litre}}{0·466 \text{ litre}}$

$= 124·5$ grams at N.T.P.

Hence, the approximate molecular weight of the compound is 124·5.

Now, we can write the equation

the molecular weight of $(C_2H_4Cl)_n = 124·5$

$\therefore \quad (2 \times 12 + 4 \times 1 + 35·46) \times n = 124·5 \quad \therefore \quad n = \frac{124·5}{63·46} = 2.$

(since *n* must be a whole number)

$\therefore$ the molecular formula is $(C_2H_4Cl)_2$ or $C_4H_8Cl_2$ and the exact molecular weight is $63·46 \times 2 = 126·92$.

Ex. 4. Chemical analysis of a compound containing Na, S, O and H gave the following results : Na = 14·31%, S = 9·97% ; H = 6·25% and O = 69·47%. Calculate the formula of the compound on the assumption that all the hydrogen atoms in the compound are present in combination with oxygen as water of crystallisation. [C. U., '18]

Solution. Dividing the percentage of each element by its atomic weight, we get

$$Na = \frac{14·31}{23} = 0·62 \; ; \; S = \frac{9·97}{32} = 0·31 \; ; \; H = \frac{6·25}{1} = 6·25 \; ; \; O = \frac{69·47}{16} = 4·34$$

Dividing the numbers by their highest common divisor, we obtain

$$Na = \frac{0·62}{0·31} = 2 \; ; \quad S = \frac{0·31}{0·31} = 1 \; ; \quad H = \frac{6·25}{0·31} = 20 \; ; \; O = \frac{4·34}{0·31} = 14$$

Hence, the simplest formula of the compound is $Na_2SH_{20}O_{14}$. Since all the hydrogen atoms are present in combination with oxygen, 20 atoms of hydrogen combine with 10 atoms of oxygen to form 10 molecules of water. 4 atoms of oxygen are thus left. The formula of the compound is, therefore, $Na_2SO_4, 10H_2O$.

Ex. 5. On burning 4·3 grams of a hydrocarbon, 13·2 grams of carbon dioxide are evolved. The density of hydrocarbon vapour with respect to hydrogen is 43. Calculate the molecular formula of the hydrocarbon.

Solution. $\underset{12 \text{ grams}}{C} + \underset{32 \text{ grams}}{O_2} = \underset{44 \text{ grams}}{CO_2}$

44 grams of carbon dioxide contain 12 grams of carbon

$\therefore$ 13·2 grams of carbon dioxide contain $\frac{12 \times 13·2}{44} = 3·6$ grams of carbon.

The hydrocarbon, therefore, contains 3·6 grams of carbon.

Hence, the weight of hydrogen present in 4·3 grams of hydrocarbon is $4{\cdot}3-3{\cdot}6=0{\cdot}7$ gram.

Let the formula of the hydrocarbon is C_xH_y where x and y are the numbers of atoms of carbon and hydrogen respectively. Then,

$$\frac{\text{the weight of carbon}}{\text{the weight of hydrogen}}=\frac{\text{at. wt. of carbon}\times x}{\text{at. wt. of hydrogen}\times y}=\frac{12\times x}{1\times y}=\frac{3{\cdot}6}{0{\cdot}7}$$

$$\therefore\ \frac{12x}{y}=\frac{3{\cdot}6}{0{\cdot}7}\ \text{or,}\ \frac{x}{y}=\frac{3{\cdot}6}{0{\cdot}7\times12}=\frac{3}{7}$$

Hence, the empirical formula of hydrocarbon is C_3H_7 and its molecular formula is $(C_3H_7)_n$ where n is an integer. Since the vapour density of hydrocarbon is 43, its molecular weight is $43\times2=86$. Thus, we can write the equation

$$\text{molecular weight of } (C_3H_7)_n=86$$

$$\text{or,}\quad (3\times12+7\times1)n=86\qquad\therefore\ n=\frac{86}{43}=2.$$

the molecular formula of hydrocarbon is thus $(C_3H_7)_2$ or C_6H_{14}

Ex. 6. 2·24 grams of sulphur burn in oxygen to give 4·48 grams of an oxide. Calculate the formula of the oxide.

Solution. Weight of sulphur in the oxide=2·24

$\therefore$ weight of oxygen in the oxide$=4{\cdot}48-2{\cdot}24=2{\cdot}24$ gram

Let the formula of the oxide be S_xO_y where x and y are the number of atoms of sulphur and oxygen respectively.

$$\text{Then in } S_xO_y\ ;\ \frac{\text{the weight of sulphur}}{\text{the weight of oxygen}}=\frac{\text{at. wt. of sulphur}\times x}{\text{at. wt. of oxygen}\times y}$$

$$\therefore\ \frac{\text{the weight of sulphur}}{\text{at. wt. of sulphur}}:\frac{\text{wt. of oxygen}}{\text{at. wt. of oxygen}}=x:y$$

$$\text{or,}\ \frac{2{\cdot}24}{32}:\frac{2{\cdot}24}{16}=x:y\qquad\text{or,}\ \frac{2{\cdot}24}{32}\times\frac{16}{2{\cdot}24}=\frac{x}{y}=\frac{1}{2}.$$

Hence, the formula of the oxide is SO_2.

$$\text{Alternatively ;}\ \frac{\text{the weight of sulphur}}{\text{the weight of oxygen}}=\frac{32\times x}{16\times y}=\frac{2{\cdot}24}{2{\cdot}24}=1.$$

$$\therefore\ \frac{32x}{16y}=1\quad\therefore\ \frac{x}{y}=\frac{16}{32}=\frac{1}{2}.$$

Hence, the formula of the oxide is SO_2.

Ex. 7. An analysis of a mineral gave the following results

Silica	57·54%	Lime	8·95%
Alumina	16·28%	Water	17·23%

Calculate the simplest formula of the mineral (Si=28, Al=27, Ca=40, H=1, O=16).

Solution.

Molecular weight of (i) silica, $SiO_2=28+2\times16=60$

(ii) alumina, $Al_2O_3=27\times2+16\times3=102$

(iii) lime, $CaO=40+16=56$

(iv) water, $H_2O=2\times1+16=18$.

Dividing the percentage by the respective molecular weight, we get

$$SiO_2=\frac{57{\cdot}54}{60}=0{\cdot}959\ ;\ Al_2O_3=\frac{16{\cdot}28}{102}=0{\cdot}1596$$

$$CaO=\frac{8{\cdot}95}{56}=0{\cdot}1598\ ;\quad H_2O=\frac{17{\cdot}23}{18}=0{\cdot}956$$

Dividing the numbers by 0·1596, we get

$$SiO_2=\frac{0{\cdot}959}{0{\cdot}1596}=6\ ;\qquad Al_2O_3=\frac{0{\cdot}1596}{0{\cdot}1596}=1$$

$$CaO=\frac{0{\cdot}1598}{0{\cdot}1596}=1\ ;\qquad H_2O=\frac{0{\cdot}956}{0{\cdot}1596}=6$$

Hence, the simplest formula of the mineral is

$$CaO,\ Al_2O_3,\ 6SiO_2,\ 6H_2O.$$

Ex. 8. Find the percentage composition of cryolite AlF_3, 3NaF. (Al=27 ; F=19 ; Na=23).

Solution. The formula weight of cryolite

$$=(27\times1+19\times6+23\times3)=210.$$

∴ 210 parts by weight of cryolite contain 27 parts by weight of aluminium.

∴ 100 parts by weight of cryolite contain $\frac{27\times100}{210}=12{\cdot}857$

∴ Percentage of aluminium = 12·857

Similarly, percentage of fluorine $=\frac{6\times19}{210}\times100=54{\cdot}28$

percentage of sodium $=\frac{3\times23}{210}\times100=32{\cdot}85$.

Ex. 9. When a crystalline salt is made anhydrous 45·6% decrease in weight is observed. The chemical analysis of the anhydrous salt shows that it contains 10·5% of Al, 15·1% of K, 24·8% of S and 49·6% of O. Calculate the empirical formula of the crystalline and anhydrous salt. [C. U. I. Sc., H. S. '75]

Solution. The ratio of the number of atoms present in anhydrous salt is

$$\text{Al : K : S : O} = \frac{10\cdot5}{27} : \frac{15\cdot1}{39} : \frac{24\cdot8}{32} : \frac{49\cdot6}{16}$$
$$= 0\cdot388 : 0\cdot387 : 0\cdot774 : 3\cdot1$$
$$= 1 : 1 : 2 : 8$$

∴ The empirical formula of the anhydrous salt is $AlKS_2O_8$

If the empirical formula and molecular formula of the compound is the same, then the molecular weight of the anhydrous salt is

$$(27+39+64+128)=258$$

100 parts by weight of the crystalline salt contain 45·6 parts by weight of water and 54·4 parts by weight of anhydrous salt.

Hence, the ratio of the molecules of the anhydrous salt and water is

$$AlKS_2O_8 : H_2O = \frac{54\cdot4}{258} : \frac{45\cdot6}{18} \quad \left[\text{mol. wt. of water is } 18\right]$$
$$= 0\cdot21 : 2\cdot53 = 1 : 12$$

∴ the empirical formula of the crystalline salt is $AlKS_2O_8$, $12H_2O$.

Ex. 10. The percentage composition of a colourless crystalline compound is given below :

Sulphur—24·24%, nitrogen—21·21%, hydrogen—6·06% and the rest is oxygen. Determine the empirical formula of the compound. Name the compound if it is a sulphate and its empirical formula and molecular formula is the same, S=32, O=16. [H. S., '61]

Solution. Percentage of oxygen = 100 − (24·24 + 21·21 + 6·06) = 48·49.

The ratio of the number of atoms in the compound,

$$\text{S : N : H : O} = \frac{24\cdot24}{32} : \frac{21\cdot21}{14} : \frac{6\cdot06}{1} : \frac{48\cdot49}{16}$$
$$= 0\cdot757 : 1\cdot515 : 6\cdot06 : 3\cdot03$$
$$= 1 : 2 : 8 : 4$$

Hence, the empirical formula of the compound is $SN_2H_8O_4$.

Since the compound is a sulphate it contains the sulphate (SO_4) radical. As the empirical formula and molecular formula is the same, the molecular formula of the compound is $SN_2H_8O_4$ or $(NH_4)_2\,SO_4$. Hence, the name of the compound is ammonium sulphate.

Ex. 11. A compound of carbon, hydrogen and nitrogen contains three elements in the respective ratio of 9 : 1 : 3·5 grams. Calculate its empirical formula. If its molecular weight is 108, what is its molecular formula ? [I. I. T., '73]

Solution. $\text{C : H : N} = \frac{9}{12} : \frac{1}{1} : \frac{3\cdot5}{14}$

$$= 0\cdot75 : 1 : 0\cdot25 = 3 : 4 : 1$$

$\therefore$ Empirical formula $= C_3H_4N$

Its molecular formula $= (C_3H_4N)_x$

$\therefore$ $(3\times12+4+14)x=108$ $\therefore$ $x=2$

$\therefore$ The molecular formula of the compound is $C_6H_8N_2$.

Ex. 12. When 2 grams of phosphorus is burnt in oxygen 3·54 grams of oxide are formed. What is the empirical formula of the oxide ? Calculate the molecular formula of the oxide if its vapour density is 110. [P=31]

Solution. The weight of phosphorus $=2$ grams
The weight of oxygen $=3{\cdot}54-2=1{\cdot}54$ grams.

Let us suppose that the formula of the oxide is $PxOy$ where x is the number of phosphorus atoms and y is the number of oxygen atoms. Hence in $PxOy$,

$$\frac{\text{weight of phosphorus}}{\text{weight of oxygen}}=\frac{\text{atomic weight of phosphorus}\times x}{\text{atomic weight of oxygen}\times y}$$

$$\frac{2}{1{\cdot}54}=\frac{31\times x}{16\times y} \qquad \therefore \frac{x}{y}=\frac{2}{3}$$

$\therefore$ The empirical formula of the oxide is P_2O_3

$\therefore$ The molecular formula of the oxide $=(P_2O_3)_n$ where n is a whole number.

Its molecular weight $=110\times2=220$

$\therefore$ $(2\times31+3\times16)\times n=220$ $\therefore$ $n=2$

Hence, the molecular formula of the oxide is twice its empirical formula and molecular formula is P_4O_6.

EXERCISE

1. What do you mean by empirical formula ? [H. S., '67, '70]

2. What do you mean by molecular formula ? [H. S., '70]

3. How are empirical formula and molecular formula determined from percentage composition ?

4. Chemical analysis of an oxide of iron shows that it contains 77·7% of iron and 22·3% of oxygen. Calculate the empirical formula of the oxide. (Fe=56) [Ans. FeO]

5. Calculate the empirical formula of a compound containing 43·4% of sodium, 11·3% of carbon and 45·3% of oxygen. (Na=23) [Ans. Na_2CO_3]

6. An analysis of a compound containing potassium, sulphur and oxygen shows that it contains 44·8% of potassium and 18·4% of sulphur. Calculate the simplest formula of the compound. (K=39, S=32) [Ans. K_2SO_4]

7. A hydrocarbon contains 93·75% of carbon, and 6·25% of hydrogen. Its vapour density is 64. Calculate the molecular formula of the hydrocarbon. [Ans. $C_{10}H_8$]

8. Chemical analysis of a chloride of silicon gives the following results :

$$Si = 16{\cdot}46\% \ ; \ Cl = 83{\cdot}54\%$$

The vapour density of the chloride is 85 (H=1). What is the molecular formula of silicon chloride ? (Si=28) [Ans. $SiCl_4$]

9. An analysis of chloride of carbon gives the following percentage composition. C=7·8%, Cl=92·2%

Its vapour density is 77 (H=1). Assuming that each molecule of the chloride contains one atom of carbon, calculate from these data, the atomic weight of carbon (Cl=35·5) [Ans. 12]

10. A compound consisting of nitrogen, hydrogen, and oxygen contains 35% of nitrogen and 5% of hydrogen. When heated, it evolves a gas which contains 63·63% of nitrogen and 36·37% of oxygen. Calculate the simplest formula of each. [Ans. NH_4NO_3, N_2O]

11. A compound contains 10·05% of carbon, 0·84% of hydrogen and 89·1% of chlorine. When vaporised 0·8575 gram of the compound occupy 250 c.c. at 150°C and 760 mm. pressure. Calculate the molecular formula of the compound. [Ans. $CHCl_3$]

12. A gaseous hydrocarbon contains 80% of carbon and 20% of hydrogen. 500 c.c. of the gas at N. T. P. weigh 0·678 gram. What is the formula of the gas ? [Ans. C_2H_6]

13. On burning an organic compound consisting of carbon, hydrogen and sulphur, 2·64 grams of carbon dioxide, 1·62 grams of water and 1·92 grams of sulphur dioxide were obtained. What is the formula of the organic compound ? [Ans. C_2H_6S]

14. 26·4 grams of carbon dioxide and 16·2 grams of water were obtained when 13·8 grams of an organic compound were completely burnt. The vapour density of the compound is 23 (H=1). What is its molecular formula ? [Ans. C_2H_6O]

15. Two oxides of a metal contain 7·17% and 13·39% of oxygen respectively. If the formula of the first be MO find that of the second. [Ans. MO_2]

16. 0·5 gram of phosphorus gave 1·145 grams of an oxide on burning. What is the simplest formula of the oxide ? [Ans. P_2O_5]

17. An element forms two chlorides containing 77·45% and 85·13% of chlorine. If the molecular weight of the highest chloride be 208·5, calculate the valencies of the element assuming that each molecule of the chlorides contains only one atom of the element. [Ans. 3 and 5]

18. A crystalline salt on analysis shows that it contains 9·8% of magnesium, 13% of sulphur, 26% of oxygen (which is not present as water of crystallisation) and 51·2% of water. Calculate the simplest formula of the salt. (Mg=24) [Ans. $MgSO_4$, $7H_2O$]

19. Calculate the formula of Glauber's salt knowing that its 6·44 grams lose 3·6 grams of water on dehydration and leave behind Na_2SO_4. [Ans. Na_2SO_4, $10H_2O$]

20. An element, M forms a hydride containing 5·88% of hydrogen. It also forms two oxides containing 50% and 60% of oxygen respectively. If the atomic weight of the element is 32, what are the formulas of the hydride and the oxides ? [MH_2, MO_2, MO_3]

21. Carbon monoxide was passed over heated cupric oxide when 1·257 grams of CO_2 were formed and the weight of cupric oxide was decreased by 0·4563 grams. Find the formula of carbon monoxide. [Ans. CO]

22. 6·44 grams of sodium sulphate crystal lose 3·6 grams of water on heating. 1·61 grams of the crystals precipitate 1·165 grams of $BaSO_4$ when treated with barium chloride solution. Calculate the formula of the crystal. (Ba=137) [Ans. Na_2SO_4, $10H_2O$]

23. A chemical analysis of a mineral gave the following results : SiO_2=47·09% ; Al_2O_3=26·99% ; Na_2O=16·46%, K_2O=0·01% ; H_2O=9·80%.
Deduce a formula for this mineral. [Ans. Na_2O, Al_2O_3, $3SiO_2$, $2H_2O$]
(Si=28, Al=27, Na=23, K=39)

24. A monobasic inorganic acid contains 2·74% of hydrogen and 97·26% of chlorine. If 0·1825 gram of the acid neutralise 0·2 gram of caustic soda, what is the formula of the acid ? [Ans. HCl]

25. Find the percentage composition of the following compounds :
(a) $K_3[Fe(CN)_6]$ (b) KNO_3 and (c) H_2O_2.
[Ans. (a) K=35·6, Fe=17, C=21·9, N=25·5 (b) K=38·61, N=13·86 ; O=47·52 (c) H=5·90, O=94·10]

26. A chemical analysis of a compound gives the following results :
Na=12·89% ; Sb=22·8% ; S=23·93%, H_2O=40·38%.

It contains 10·09% hygroscopic moisture. Calculate the formula of the compound. (Sb=122) [Ans. Na_3SbS_4, $9H_2O$]

27. A sodium salt of an acid gives on analysis the following results :
C=29·26%, H=3·66% O=39·02% and Na=28·04%. Calculate the simplest formula of the acid. [Ans. $C_2H_4O_2$]

28. 1 gram of a compound consisting of calcium, carbon and oxygen, contains 0·48 gram of oxygen. On heating, it evolves CO_2 which occupies 224 c.c. at N.T.P. and leaves a solid which does not contain carbon. Calculate the formula of the compound. [Ans. $CaCO_3$]

29. A compound contains 1·59% hydrogen, 22·22% nitrogen and 76·19% oxygen. What is the empirical formula of the compound ?

[Ans. HNO_3] [H. S., '70]

30. The percentage composition of a salt is given below :
Na=27·38, H=1·19, C=14·29, O=57·40
What is the simplest formula of the salt ? [Ans. $NaHCO_3$] [H. S., '65]

31. A gaseous compound of carbon and nitrogen containing 53·8 per cent by weight of nitrogen was found to have a vapour density of 25·8. What is the molecular formula of the compound ? [Ans. C_2N_2] [I. I. T., '71]

32. An organic compound containing C, H and O was subjected to combustion. From 1·367 gram of the substance were obtained 3·002 gram of CO_2 and 1·640 gram of H_2O. Find out the empirical formula.

[Ans. C_3H_8O] [I. I. T., '75]

33. A compound of carbon, hydrogen and oxygen contains 40% carbon, and 6·67% hydrogen. If the molecular weight of the compound is 180, what is its molecular formula ? [H. S., '67, '70] [Ans. $C_6H_{12}O_6$]

34. A compound contains 40% carbon, 6·66% hydrogen and the rest is oxygen. What is the empirical formula of the compound ? When vapourized, its density is found to be 2·813 times that of oxygen under the same condition of temperature and pressure. Determine the molecular formula of the compound.

[Ans. $C_3H_6O_3$] [H. S., '73]

35. 1 gram of blue vitriol (molecular formula, $CuSO_4$, nH_2O) on being heated to a constant weight gives 0·638 gram of the residue. Calculate the value of n. [Ans. n=5] [H. S., '74]

36. A compound contains 10·05% carbon, 0·84% hydrogen and 89·1% chlorine. The density of the compound in the vapour state at 150°C and 760 mm. pressure is 0·00343 gram/c.c. Calculate the molecular formula of the compound. [Ans. $CHCl_3$]

37. 0·354 gram of a compound of carbon, hydrogen and nitrogen when burnt in oxygen gives 0·792 gram of CO_2 and 0·486 gram of H_2O. On chemical analysis it is further found that the same weight of the compound gives at N.T.P.

67·2 c.c. of nitrogen. If the vapour density of the compound is 29·5, what is its molecular formula ? [Ans. C_3H_9N]

38. A gaseous hydrocarbon contains 85·72% carbon, and 14·28% hydrogen. At S.T.P. the density of the gas is 0·00126 gram/c.c. Calculate its molecular formula. [Ans. C_2H_4]

39. The element E forms two gaseous hydrides A and B in which the percentages of E are respectively 75 and 81·8. The vapour densities of the hydrides are respectively 8 and 22. If the molecule of A contains one atom of E, calculate the atomic weight of E and formula of A and B. [Ans. EH_4, E_3H_8]

40. Carbohydrates are compounds containing only carbon, hydrogen and oxygen, having the atomic ratio of H : O as 2 : 1. When heated in the absence of air, these compounds decompose to form carbon and water :

(a) If 310 gram of a carbohydrate leave a residue of 124 gram of carbon on heating in absence of air, what is the empirical formula of the carbohydrate ?

(b) If 0·0833 mole of the carbohydrate contains 1·00 gram of hydrogen, what is the molecular formula of the carbohydrate ?

[Ans. (a) $C(H_2O)$ (b) $C_6H_{12}O_6$] [I. I. T., '69]

41. A certain compound containing only carbon and oxygen has an approximate molecular weight of 290. On analysis it is found to contain exactly 50 p.c. by weight of each element. What is the molecular formula of the compound ? [Ans. $C_{12}O_9$] [I. I. T., '70.]

42. 1 gram of a compound contains 0·262 gram of nitrogen, 0·075 gram of hydrogen and 0·663 gram of chlorine. What is the simplest formula of the compound ? [Ans. NH_4Cl] [H. S. (Comp.), '62.]

Calculations using equations

A chemical equation not only represents the nature of the reacting substances and the products but also expresses a definite weight relationship among the reactants and products of a reaction. For example,

$$\underset{100\text{ grams}}{CaCO_3} + \underset{2\times 36\cdot 5\text{ grams}}{2HCl} = \underset{111\text{ grams}}{CaCl_2} + \underset{18\text{ grams}}{H_2O} + \underset{44\text{ grams}}{CO_2}$$

represents the reaction between calcium carbonate and hydrochloric acid. The quantities of the five substances concerned in the reaction are calculated with the help of atomic-weight chart of the elements. The balanced equation states that 100 grams of calcium carbonate reacts with 71 grams of hydrogen chloride to produce 111 grams of calcium chloride, 18 grams of water and 44 grams of carbon dioxide. It is thus possible to determine the quantity of hydrochloric acid which will react with say 7 kilograms of calcium carbonate. Using chemical equations, we shall solve three types of problems, namely,

(i) Weight-Weight problems
(ii) Weight-Volume problems
(iii) Volume-Volume problems

In solving these problems the following relationships are utilised :

(i) Molecular weight, M = Normal density, $\rho \times 22{\cdot}4$ litres

(ii) The weight of 1 litre of a gas at N.T.P.
$=$ The vapour density of the gas $\times 0{\cdot}09$ gram

(iii) The weight of 1 litre of hydrogen at N.T.P. $= 0{\cdot}09$ gram

(iv) The volume of 1 mole of a gas at N.T.P. is 22·4 litres.

(v) Molecular weight $=$ vapour density $\times 2$

(i) **Weight-weight problems.** In these, we are given one weight and asked to find another. The following examples will illustrate the procedure of calculations.

1. What weight of carbon dioxide is obtained upon burning 2 grams of carbon monoxide in oxygen ?

Solution.
$$\underset{2(12+16)=56}{2CO} + \underset{2\times16=32}{O_2} = \underset{2(12+2\times16)=88}{2CO_2}$$

56 grams of carbon monoxide upon burning yield 88 grams of carbon dioxide.

$\therefore$ 2 grams of carbon monoxide upon burning yield $\dfrac{88\times2}{56}$

$= 3{\cdot}143$ grams of carbon dioxide.

2. How much potassium chlorate will be just required to produce 5 grams of oxygen ? (K=39) [H. S. (Comp.), '71]

Solution.
$$\underset{2\times122{\cdot}5}{2KClO_3} = 2KCl + \underset{3\times32}{3O_2}$$

$\therefore$ 96 grams of oxygen are obtained from 245 grams of $KClO_3$.

$\therefore$ 5 grams of oxygen are obtained from $\dfrac{245\times5}{96}$

$= 12{\cdot}76$ grams of $KClO_3$.

3. How much potassium chlorate must be heated to yield as much oxygen as would be obtainable from 500 grams of mercuric oxide ? (K=39, Hg=200)

Solution.
$$\underset{432}{2HgO} = 2Hg + \underset{32}{O_2}$$

432 grams of mercuric oxide produce 32 grams of oxygen.

$\therefore$ 500 grams of mercuric oxide produce $\dfrac{32\times500}{432} = 37{\cdot}0$ grams of oxygen.

Now,
$$\underset{245}{2KClO_3} = 2KCl + \underset{96}{3O_2}$$

96 grams of oxygen are obtained from 245 grams of $KClO_3$

$\therefore$ 37 grams of oxygen are obtained from $\dfrac{245\times37}{96}$

$= 94{\cdot}42$ grams of $KClO_3$

4. How much zinc will be required to produce hydrogen which is just sufficient to combine completely with oxygen obtained by heating 10 grams of potassium chlorate. (Zn = 65·3)

Solution. $\underset{245}{2KClO_3} = 2KCl + \underset{96}{3O_2}$

245 grams of $KClO_3$ yield 96 grams of oxygen

∴ 10 grams of $KClO_3$ yield $\frac{96 \times 10}{245} = 3{\cdot}92$ grams of oxygen

$$\underset{4}{2H_2} + \underset{32}{O_2} = 2H_2O$$

32 grams of oxygen combine with 4 grams of hydrogen

∴ 3·92 grams of oxygen combine with $\frac{4 \times 3{\cdot}92}{32} = 0{\cdot}49$ grams of hydrogen

$$\underset{65{\cdot}3}{Zn} + H_2SO_4 = ZnSO_4 + \underset{2}{H_2}$$

To prepare 2 grams of hydrogen 65·3 grams of zinc are required

∴ To prepare 0·49 grams of hydrogen $\frac{65{\cdot}3 \times 0{\cdot}49}{2} = 15{\cdot}998$ grams of zinc are required.

5. 5 grams of pure manganese dioxide (MnO_2) are heated with excess of conc. HCl. The evolved gas is passed into a solution of KI. Calculate the weight of iodine liberated. (Mn=55, I=127)

Solution. $\underset{87}{MnO_2} + 4HCl = MnCl_2 + 2H_2O + \underset{71}{Cl_2}$

∴ 87 grams of MnO_2 produce 71 grams of chlorine

∴ 5 grams MnO_2 produce $\frac{71 \times 5}{87} = 4{\cdot}08$ grams of chlorine

$$2KI + \underset{71}{Cl_2} = 2KCl + \underset{254}{I_2}$$

71 grams of chlorine liberate 254 grams of iodine

∴ 4·08 grams of chlorine liberate $\frac{254 \times 4{\cdot}08}{71} = 14{\cdot}596$ grams

∴ the weight of iodine liberated = 14·596 grams.

6. What weight of chalk must be decomposed by HCl to produce a quantity of carbon dioxide that is just sufficient to convert 200 grams of sodium hydroxide to sodium carbonate ? (Ca=40)

Solution. $\underset{80}{2NaOH} + \underset{44}{CO_2} = Na_2CO_3 + H_2O$

80 grams of sodium hydroxide react with 44 grams of CO_2

∴ 200 grams of sodium hydroxide react with $\frac{44\times200}{80}=110$ grams of CO_2

$$\underset{100}{CaCO_3}+2HCl=CaCl_2+H_2O+\underset{44}{CO_2}$$

44 grams of CO_2 are obtained by the decomposition of 100 grams of $CaCO_3$

∴ 110 grams of CO_2 are obtained by the decomposition of $\frac{100\times110}{44}$ $=250$ grams of $CaCO_3$

∴ the weight of chalk required=250 gram.

7. 1·84 grams of a mixture of $CaCO_3$ and $MgCO_3$ are strongly heated till no further loss in weight takes place. The residue weighs 0·96 gram. Determine the percentage composition of the mixture. [A. U. '38, U. P. Board, '43]

Solution. Let us suppose that the weight of $CaCO_3$ in the mixture is x grams. Then the weight of $MgCO_3=(1{\cdot}84-x)$ grams When heated, calcium carbonate decomposes into lime and carbon dioxide, i.e.,

$$\underset{100}{CaCO_3}=\underset{56}{CaO}+CO_2$$

∴ 100 grams of $CaCO_3$ give 56 grams of CaO as residue

∴ x grams of $CaCO_3$ give $\frac{56\times x}{100}$ grams of CaO as residue.

Magnesium carbonate when heated decomposes into magnesium oxide and carbon dioxide.

$$\underset{84}{MgCO_3}=\underset{40}{MgO}+CO_2$$

84 grams of $MgCO_3$ give 40 grams of MgO as residue

∴ $(1{\cdot}84-x)$ grams of $MgCO_3$ give $\frac{40\times(1{\cdot}84-x)}{84}$ grams of MgO as residue

$$\therefore\ \frac{56x}{100}+\frac{40\times(1{\cdot}84-x)}{84}=0{\cdot}96$$

Solving for x, we get $x=1$

∴ 1·84 grams of the mixture contain 1 gram of $CaCO_3$

∴ 100 grams of the mixture contain $\frac{1}{1{\cdot}84}\times100=54{\cdot}35$

∴ percentage of $CaCO_3=54{\cdot}35$

Now, 1·84 grams of the mixture contain (1·84 − 1)=0·84 grams of $MgCO_3$

∴ 100 grams of the mixture contain $\frac{0{\cdot}84 \times 100}{1{\cdot}84}=45{\cdot}65$ grams of $MgCO_3$

∴ percentage of $MgCO_3=45{\cdot}65$.

8. A quantity of a mixture of potassium iodide and chloride is converted into potassium sulphate and the weight of the sulphate is found to be the same as that of the original mixture. In what proportions were the salts present in the mixture ?

(K=39·1, Cl=35·4, I=126·9. S=32, O=16)

Solution. The equations involved are

$$\underset{332}{2KI}+H_2SO_4=\underset{174{\cdot}2}{K_2SO_4}+2HI$$

whence 332 grams of potassium iodide give 174·2 grams of potassium sulphate.

$$\underset{149}{2KCl}+H_2SO_4=\underset{174{\cdot}2}{K_2SO_4}+2HCl$$

whence 149 grams of potassium chloride give 174·2 grams of potassium sulphate.

Let 100 grams be the weight of the mixture of potassium chloride and iodide and 'a' grams be the weight of potassium chloride.

Then the weight of potassium iodide=(100 − a) grams and the weight of potassium sulphate formed would also be 100 grams according to the conditions of the problem.

332 grams of KI give 174·2 grams of K_2SO_4

∴ (100 − a) grams of KI give $\frac{174{\cdot}2}{332}\times(100-a)$ grams of K_2SO_4

149 grams of KCl give 174·2 grams of K_2SO_4

∴ a grams of KCl give $\frac{174{\cdot}2\times a}{149}$ grams of K_2SO_4

∴ the weight of the mixed sulphate is

$$\frac{174{\cdot}2\times(100-a)}{332}+\frac{174{\cdot}2\times a}{149}=100$$

Solving for a, we get a=73·8

∴ 100 grams of the mixture of potassium chloride and iodide contain 73·8 grams of potassium chloride and 100 − 73·8=26·2 grams of potassium iodide.

∴ percentage of KCl=73·8 ; percentage of KI=26·2.

9. 3 grams of a mixture of sodium chloride and potassium iodide were dissolved in water and a solution of silver nitrate was added to it until the precipitation was complete. The washed and dried precipitate of silver chloride and iodide weighed 5·8 grams. What was the percentage of each salt in the mixture ?

Solution. Let the weight of NaCl in the mixture be x grams. Then the weight of KI$=(3-x)$ grams. Now, the equations involved are : $\underset{58{\cdot}5}{NaCl}+AgNO_3=\underset{143{\cdot}5}{AgCl}+NaNO_3$; $\underset{166}{KI}+AgNO_3=\underset{235}{AgI}+KNO_3$

$\therefore$ 58·5 grams of NaCl give 143·5 grams of AgCl

x grams of NaCl give $\frac{143{\cdot}5\times x}{58{\cdot}5}$ grams of AgCl

166 grams of KI give 235 grams of AgI

$\therefore$ $(3-x)$ grams of KI give $\frac{235\times(3-x)}{166}$ grams of AgI

The weight of the mixed precipitate of AgCl and AgI is

$$\frac{143{\cdot}5\times x}{58{\cdot}5}+\frac{235\times(3-x)}{166}=5{\cdot}8$$

Solving for x, we get $x=1{\cdot}497$ grams

$\therefore$ the weight of NaCl is 1·497 grams

Hence, the weight of KI$=1{\cdot}503$ grams

$\therefore$ percentage of NaCl$=49{\cdot}9$, percentage of KI$=50{\cdot}1$

10. 5 grams of strontium chloride containing 6 molecules of water of crystallisation gave 3·442 grams of strontium sulphate. Calculate the atomic weight and the equivalent weight of strontium. (O=16, S=32, Cl=35·5)

Solution. Let a be the atomic weight of strontium. Then the gram-molecular weight of $SrCl_2\ 6H_2O$ is (a+179) grams and that of strontium sulphate $SrSO_4$ is (a+96) grams. (a+179) grams of $SrCl_2 6H_2O$ contain a grams of strontium

$\therefore$ 5 grams of $SrCl_2$, $6H_2O$ contain $\frac{a\times5}{a+179}$ grams of strontium.

(a+96) grams of $SrSO_4$ contain a grams of strontium

3·442 grams of $SrSO_4$ contain $\frac{a\times3{\cdot}442}{a+96}$ grams of strontium

Hence, $\frac{a\times5}{a+179}=\frac{a\times3{\cdot}442}{a+96}$ whence a$=87{\cdot}37$

Hence, the atomic weight of strontium is 87·37 and its equivalent weight is $\frac{87{\cdot}37}{2}=43{\cdot}7$ since valency of strontium is 2.

11. How much pyrolusite containing 80% manganese dioxide will be required to liberate from hydrochloric acid a quantity of chlorine which is just sufficient to convert 20 grams of sodium hydroxide completely into chlorate and chloride ?

Solution. $\underset{213}{3Cl_2}+\underset{240}{6NaOH}=5NaCl+NaClO_3+3H_2O$

240 grams of sodium hydroxide react with 213 grams of chlorine

20 grams of sodium hydroxide react with $\frac{213 \times 20}{240}$

$= 17{\cdot}75$ grams of chlorine

$$\underset{87}{MnO_2} + 4HCl = MnCl_2 + 2H_2O + \underset{71}{Cl_2}$$

71 grams of chlorine are liberated by 87 grams of MnO_2

∴ 17·75 grams of chlorine are liberated by $\frac{87 \times 17{\cdot}75}{71}$

$= 21{\cdot}74$ grams of MnO_2

Now, 80 grams of MnO_2 are present in 100 grams of pyrolusite

21·74 grams of MnO_2 are present in $\frac{100 \times 21{\cdot}75}{80}$

$= 27{\cdot}187$ grams of pyrolusite

∴ the amount of pyrolusite required is 27·187 grams.

12. Hydrogen prepared by the action of sulphuric acid on 15 grams of zinc is passed separately over (i) 5 grams of dry cupric oxide and (ii) 25 grams of cupric oxide. What will be the weight of the residue and its composition in each case ? (Zn=65 ; Cu=63)

Solution. $\underset{65}{Zn} + H_2SO_4 = ZnSO_4 + \underset{2}{H_2}$

65 grams of zinc liberate 2 grams of hydrogen

∴ 15 grams of zinc liberate $\frac{2 \times 15}{65} = 0{\cdot}4615$ grams of hydrogen

$$\underset{79}{CuO} + \underset{2}{H_2} = \underset{63}{Cu} + H_2O$$

2 grams of hydrogen reduce 79 grams of CuO to form 63 grams of Cu

∴ 0·4615 grams of hydrogen reduce $\frac{79 \times 0{\cdot}4615}{2} = 18{\cdot}23$ grams of CuO to form $\frac{63 \times 0{\cdot}4615}{2}$ grams of Cu

∴ 0·4615 gram of hydrogen reduce $\frac{79}{2} \times 0{\cdot}4615$ or 18·23 grams of CuO to form $\frac{63}{2} \times 0{\cdot}4615$ or 14·54 grams of Cu.

(i) In this case, all cupric oxide is reduced by hydrogen to metallic copper.

Now, 79 grams of CuO are reduced to 63 grams of Cu

∴ 5 grams of CuO are reduced to $\frac{63 \times 5}{79} = 3{\cdot}985$ grams of Cu

(ii) In this case, all hydrogen is used up in reducing cupric oxide and there remains excess of cupric oxide.

Now, 0·4615 gram of hydrogen reduce 18·23 grams of CuO to form 14·54 grams of copper.

∴ Amount of CuO which are not reduced is 25 – 18·23 = 6·77 grams

Hence, the residue contains 14·54 grams of Cu and 6·77 grams of CuO. The weight of the residue is 21·31 grams.

13. Calculate the weight of calcium nitrate formed in the reaction of 100 grams of nitric acid and 60 grams of calcium oxide. [H. S., '67]

$$\underset{56}{CaO} + \underset{2\times63}{2HNO_3} = \underset{164}{Ca(NO)_2} + H_2O$$

56 grams of CaO react with 126 grams of HNO_3

∴ 60 grams of CaO react with $\frac{126\times60}{56}=135$ grams of nitric acid

But only 100 grams of HNO_3 are given. Hence, 100 grams of nitric acid will be completely consumed in the reaction. Now,

126 grams of HNO_3 form 164 grams of $Ca(NO_3)_2$

∴ 100 grams of HNO_3 form $\frac{164\times100}{126}$

$=130·16$ grams of $Ca(NO_3)_2$

Hence, the weight of $Ca(NO_3)_2$ formed in the reaction is 130·16 grams

14. Equal weights of mercury and iodine are allowed to react completely to form a mixture of mercurous and mercuric iodides. Calculate the ratio of the weights of mercurous and mercuric iodides formed. [I. I. T., '66]

Let the weight of Hg_2I_2 formed be x gram and the weight of HgI_2 formed be y grams.

$$\begin{array}{ccccc} 2Hg & + & I_2 & = & Hg_2I_2 \\ 2\times201 & & 2\times127 & & 2\times(201+127) \\ 201 & & 127 & & 328 \end{array}$$

∴ 328 grams of Hg_2I_2 are formed from 201 grams of Hg and 127 grams of I_2

∴ x grams of Hg_2I_2 are formed from $\frac{201\times x}{328}$ gram of Hg and $\frac{127\times x}{328}$ gram of I_2

$$\begin{array}{ccccc} Hg & + & I_2 & = & HgI_2 \\ 201 & & 254 & & 455 \end{array}$$

∴ 455 grams of HgI_2 are formed from 201 grams of Hg and 254 grams of I_2

$\therefore$ y grams of HgI_2 are formed from $\frac{201y}{455}$ grams of Hg and $\frac{254\times y}{455}$ grams of I_2

$$\therefore \text{ Total weight of Hg}=\frac{201\times x}{328}+\frac{201\times y}{455}$$

$$\text{Total weight of } I_2=\frac{127x}{328}+\frac{254\times y}{455}$$

According to the condition of the problem,

$$\frac{201x}{328}+\frac{201y}{455}=\frac{127x}{328}+\frac{254y}{455}$$

$$\frac{201x}{328}-\frac{127x}{328}=\frac{254y}{455}-\frac{201y}{455}$$

$$\frac{74}{328}\times x=\frac{53}{455}\times y$$

$$\therefore \frac{x}{y}=\frac{53\times 328}{74\times 455}=\frac{1}{1{\cdot}936}.$$

Hence, the ratio of mercurous to mercuric iodide=1·936 : 1.

15. 25·4 grams of iodine and 14·2 grams of chlorine are made to react completely to yield a mixture of ICl and ICl_3. Calculate the ratio of the moles of ICl and ICl_3 formed. [I. I. T., '70]
(I=127, Cl=35·5)

$$\text{Number of moles of } I_2=\frac{25{\cdot}4}{254}=\frac{1}{10}$$

$$\text{Number of moles of } Cl_2=\frac{14{\cdot}2}{71}=\frac{2}{10}$$

Let us suppose that x moles of ICl and y moles of ICl_3 are formed

$$\begin{array}{llllll} I_2 & + & Cl_2 & = & 2ICl \\ \frac{x}{2}\text{ mole} & & \frac{x}{2}\text{ mole} & & x \text{ mole} \\ I_2 & + & 3Cl_2 & = & 2ICl_3 \\ \frac{y}{2}\text{ mole} & & \frac{3y}{2}\text{ mole} & & y \text{ mole} \end{array}$$

$$\therefore \text{ Number of moles of iodine}=\frac{x}{2}+\frac{y}{2}=\frac{1}{10}$$

$$\text{Number of moles of chlorine}=\frac{x}{2}+\frac{3y}{2}=\frac{2}{10}$$

$$\therefore \quad x+y=\frac{2}{10} \qquad \text{(i)}$$

$$x+3y=\frac{4}{10} \qquad \text{(ii)}$$

$$\therefore \quad 2y=\frac{2}{10} \quad \left[\text{Subtracting (i) from (ii)}\right]$$

$$\therefore \quad y=\frac{1}{10}$$

$$\therefore \quad x=\frac{2}{10}-\frac{1}{10}=\frac{1}{10}$$

$\therefore$ Ratio of the moles of ICl and ICl_3 formed is 1 : 1.

16. When a mixture of FeO and Fe_3O_4 was heated in air to a constant weight, its increase in weight was 5%. What was the percentage composition of the mixture before heating? [I. I. T., '78]

(Fe=55·8, O=16)

Let us suppose that 100 grams of the mixture contains x gram of FeO.

$\therefore$ Amount of $Fe_3O_4=(100-x)$ gram.

$$\underset{4\times(55\cdot8+16)}{4FeO} + O_2 = \underset{2\times(55\cdot8\times2+3\times16)}{2Fe_2O_3}$$

$4\times71\cdot8$ grams of FeO form $2\times159\cdot6$ grams of Fe_2O_3

$\therefore$ x gram of FeO form $\dfrac{2\times159\cdot6\times x}{4\times71\cdot8}=\dfrac{159\cdot6x}{143\cdot6}$ grams of Fe_2O_3

Again, $\underset{4\times231\cdot4}{4Fe_3O_4}+O_2 = \underset{6\times159\cdot6}{6Fe_2O_3}$

$4\times231\cdot4$ gram of Fe_3O_4 form $6\times159\cdot6$ gram of Fe_2O_3

$\therefore$ $(100-x)$ gram of Fe_3O_4 form $\dfrac{6\times159\cdot6\times(100-x)}{4\times231\cdot4}$

$$=\frac{478\cdot8(100-x)}{462\cdot8} \text{ gram of } Fe_2O_3$$

According to the condition of the problem,

$$\frac{159\cdot6x}{143\cdot6}+\frac{478\cdot8(100-x)}{462\cdot8}=105$$

Solving we get, $x=20$

Hence, the mixture contains 20% of FeO and 80% of Fe_3O_4.

17. A sample of zinc contains some impurities which do not react with hydrochloric acid. 25 grams of the sample of zinc react completely with 40 c.c. of hydrochloric acid. The specific gravity of the acid is 1·25 and it contains 50% by weight of HCl. Calculate the percentage of pure zinc and impurities in the sample. Zn=65.

Specific gravity of the acid is 1·25

∴ The weight of 1 c.c of hydrochloric acid $=1{\cdot}25$ grams

∴ The weight of 40 c.c. of hydrochloric acid $=1{\cdot}25\times 40=50$ grams.

100 grams of the aqueons solution of the acid contain 50 grams of HCl.

∴ 50 grams of the aqueous solution of the acid contain 25 grams of HCl.

$$\begin{array}{ccccccc} Zn & + & 2HCl & = & ZnCl_2 & + & H_2 \\ 65 & & 2\times 36{\cdot}5 & & & & \end{array}$$

73 grams of HCl react with 65 grams of Zn

∴ 25 grams of HCl react with $\frac{65\times 25}{73}=22{\cdot}26$ grams of Zn

But 25 grams of the sample of Zn react with 40 c.c. of hydrochloric acid

∴ 25 grams of the sample of Zn contain $25-22{\cdot}26=2{\cdot}74$ grams of impurities

∴ 100 grams of the sample of Zn contain $\frac{2{\cdot}74\times 100}{25}$

$=10{\cdot}96$ grams of impurities

∴ % Zn $=89{\cdot}04$ and % impurities $=10{\cdot}96$.

18. (a) Calculate the change in weight when 1 gram of calcium carbonate ($CaCO_3$) is heated.

(b) What will be the change in weight when 1 gram of magnesium is heated in air? $Ca=40$, $C=12$, $O=16$, $Mg=24$

(a) $$\begin{array}{ccccc} CaCO_3 & = & CaO & + & CO_2 \\ 100 & & 56 & & \end{array}$$

100 grams of $CaCO_3$ form 56 grams of CaO

∴ 1 gram of $CaCO_3$ form $0{\cdot}56$ grams of CaO

∴ Decrease in weight $=1-0{\cdot}56=0{\cdot}44$ gram

(b) $$\begin{array}{ccccc} 2Mg & + & O_2 & = & 2MgO \\ 2\times 24 & & & & 2\times 40 \end{array}$$

48 grams of magnesium give 80 grams of MgO

∴ 1 gram of magnesium give $\frac{80}{48}=1{\cdot}667$ gram of MgO

∴ Increase in weight $=1{\cdot}667-1=0{\cdot}667$ gram.

Problems

1. Find the weight of calcium oxide and carbon dioxide formed when 500 grams of calcium carbonate are strongly heated. [Ans. 280 grams ; 220 grams]

2. How much mercuric oxide would you take to prepare 2 grams of oxygen? ($Hg=201$) [Ans. 27·12 grams]

3. How much potassium chlorate must be heated to yield as much oxygen as would be obtainable from 100 grams of mercuric oxide? ($Hg=201$) [Ans. 18·7986 grams]

4. 250 c.c. of a solution of sulphuric acid was exaclty neutralised by 32·0 grams of anbydrous sodium carbonate. Express the composition of the acid solution in terms of grams of sulphuric acid per litre. [118·32 grams/litre]

5. What weight in grams of sodium hydroxide is required to convert 50 grams of copper sulphate into copper hydroxide ? [Ans. 25 grams]

6. Air contains 23 per cent by weight of oxygen. How much phosphorus must be burnt to remove oxygen completely from 2,000 grams of air.

What would be the weight of the residual gas ?

[Ans. 356·50 grams ; 1643·5 grams]

7. Calculate the weight of calcium nitrate formed by dissolving 120 grams of calcium oxide in 100 grams of nitric acid. [Ans. 130·16 grams]

[**Hints :** $\underset{56}{CaO}+\underset{126}{2HNO_3}=\underset{164}{Ca(NO_3)_2}+H_2O$

It is found that 120 grams of calcium oxide require $\frac{126\times120}{56}=270$ grams of nitric acid. But there are only 100 grams of nitric acid. So calculate the amount of calcium nitrate formed from 100 grams of nitric acid and not from 120 grams of CaO.]

8. Hydrogen is prepared by the action of Zn on H_2SO_4. What weight of zinc would be required to produce sufficient hydrogen to completely react with oxygen obtained by heating 40 grams of $KClO_3$? [Ans. 63·994 grams]

9. On dissolution of 0·8 gram of zinc dust (zinc powder containing small quantity of zinc oxide) in dilute sulphuric acid, 0·024 gram of hydrogen was liberated. Calculate the percentage of zinc in zinc dust. [Ans. 97·95%]

10. How much pyrolusite containing 82 per cent manganese dioxide will be required to furnish chlorine from HCl which will liberate 127 grams of iodine from potassium iodide solution ? [Ans. 53·07 grams]

11. A quantity of a mixture of potassium iodide and sodium chloride was converted into the normal sulphates by evaporation with sulphuric acid. If the mixture of the sulphates is found to weigh the same as the original salts, what was the composition of the original mixture ? [Ans. KI=31% NaCl=69%]

12. 2 grams of a mixture of sodium chloride and potassium chloride are converted into sulphates by evaporation with sulphuric acid, the mixture of the sulphates weighing 2·4 grams. Calculate the composition of the mixture.

[Ans. NaCl=1·391 grams KCl=1·009 grams]

13. How much pyrolusite containing 82% of MnO_2 and how much hydrochloric acid containing 33% of hydrogen chloride will be required to furnish the chlorine necessary to convert 40 grams of potassium hydroxide completely into chlorate and chloride ? [Ans. 38 grams 158 grams]

14. A sample of coal contained 2 per cent of nitrogen. The ammonia evolved on heating 200 kilograms of this coal was absorbed in sulphuric acid, the weight of ammonium sulphate formed was 2·5 kgs. What percentage of the nitrogen was evolved from the coal as ammonia ? [Ans. 6·63%]

15. How much of zinc will be required to liberate hydrogen from sulphuric acid in order to reduce completely 5 grams of cupric oxide ?

[Ans. 4·0885 grams]

16. Sea-water has a density of 1·04. How much sulphuric acid would be required to convert common salt obtained from 1 litre of sea-water completely into sodium sulphate ? Sea-water contains 3% by weight of common salt.

[Ans. 26·133 grams]

17. 50 ml of a sample of hydrochloric acid having density 1·4 was treated with 10 grams of marble. After the reaction was complete, the unreacted marble was filtered off, washed, dried and was found to weigh 5 grams. Calculate the percentage strength of the acid. [Ans. 5·214%]

18. 20 ml of a sample of hydrobromic acid having density 1·05 gave 3·8 grams of silver bromide on treatment with silver nitrate solution. Calculate the amount of HBr in 100 ml and in 100 grams of the solution.
(H=1, Br=80, Ag=108) [Ans. 8·189 grams, 7·799 grams]

19. What weight of chalk must be decomposed with HCl to produce a quantity of carbon dioxide which is just sufficient to convert 40 grams of sodium hydroxide into sodium carbonate ? [Ans. 50 grams]

20. A sample of chalk is contaminated with clay which loses 10% of its weight on heating due to the elimination of moisture. When 2 grams of this sample of chalk are heated, it loses 0·5 gram in weight. What is the percentage of chalk in the sample ? [Ans. 44.1%]

[**Hints :** Let x grams be the weight of chalk present in 2 grams of the sample. The amount of clay is $(2-x)$ gram.

$$\underset{100}{CaCO_3} = CaO + \underset{44}{CO_2}$$

$\therefore$ x gram of chalk lose $\frac{44 \times x}{100}$ grams on heating

100 grams of clay lose 10 grams on heating. $\therefore$ $(2-x)$ grams of clay lose $\frac{10 \times (2-x)}{100}$ grams on heating.

$$\therefore \quad \frac{44 \times x}{100} + \frac{10 \times (2-x)}{100} = 0{\cdot}5.$$ Hence, etc.]

21. What will be the change in weight when 1 gram of potassium chlorate is heated. Also calculate the change in weight when 1 gram of calcium carbonate is heated. [Ans. 0·3918 gram and 0·44 gram] [H. S., '71]

22. A sample of coal contains 85% carbon, 5% hydrogen, and 10% oxygen. 1 gram of the sample is burnt in dry and carbon dioxide-free air and the products are first passed through a U-tube containing anhydrous $CaCl_2$ and then through U-tube containing soda-lime. Determine the change in weight of the U-tubes. [Ans. Increase in weight of soda-lime tube=4·675 gram. Increase in weight of $CaCl_2$-tube=0·675 gram] [P. U., '63]

23. Calculate the weight of potassium chlorate required to liberate the same amount of oxygen as is obtained when 100 grams of mercuric oxide is heated. Hg=200, K=39, Cl=35·5, O=16. [Ans. 18·9 gram] [H. S., '67]

24. Calculate the weight of zinc which is required to liberate hydrogen which is just sufficient to react with the amount of oxygen obtained by heating 24·5 gram of potassium chlorate. Hydrogen is prepared by the action of zinc on excess of dil. H_2SO_4. Zn=63·5, K=39, Cl=35·5, O=16, H=1
[Ans. 39·18 gram] [P. U., '61]

25. A 2·00 gram sample containing Na_2CO_3 and $NaHCO_3$ loses 0·248 gram when heated to 300°C, the temperature at which $NaHCO_3$ decomposes to Na_2CO_3, CO_2 and water. What is the percentage of Na_2CO_3 in the mixture ?
Na=23, C=12, O=16
[Ans. $NaHCO_3$=33·6% and Na_2CO_3=66·4%] [I. I. T., '77]

26. Calculate the weight of lime (CaO) that can be prepared by heating 200 kg. of lime-stone ($CaCO_3$) which is 95% pure. [I. I. T., '75]
Ca=40, C=12, O=16 [Ans. 106·4 grams]

27. 10 grams of a mixture of copper and cupric oxide when reduced by hydrogen give 8·384 grams of copper. Calculate the percentage of copper in the mixture. Cu=63·5, O=16, H=1. [Ans. 20%]

28. One litre of an acidified solution of $KMnO_4$ containing 15·8 grams of $KMnO_4$ is decolourised by passing sufficient amount of SO_2. If the SO_2 is produced by roasting of iron pyrites (FeS_2) what will be the amount of pyrites

required to produce the necessary amount of SO_2? Fe=56, S=32, O=16, K=39, Mn=55 [Ans. 15 grams] [I. I. T., '74]

[**Hints** : $4FeS_2+11O_2=2Fe_2O_3+8SO_2$
$2KMnO_4+5SO_2+2H_2O=K_2SO_4+2MnSO_4+2H_2SO_4$]

29. 10 grams of metallic zinc was added to 200 c.c. of copper sulphate solution. After all the copper was precipitated it was found that not all the zinc has dissolved. After filtration, the total weight of the solid at the end of the reaction was 9·81 gram. Calculate the weight of copper deposited. Cu=63·5, Zn=65·4 [Ans. 6·35 gram] [I. I. T., '71]

30. The oxides of sodium and potassium contained in a 0·5 gram sample of feldspar were converted to the respective chlorides. The weight of the chlorides thus obtained was 0·1180 gram. Subseqent treatment of the chlorides with silver nitrate gave 0·2451 gram of silver chloride. What is the percentage of Na_2O and K_2O in the sample ? Ag=108, Cl=35·5, Na=23, K=39 [Ans. Na_2O=3·577%, K_2O=10·62%] [I. I. T., '68]

31. When heated 10 gram of a mixture of potassium chlorate and potassium chloride give 8 grams of the residue. Calculate the percentage of potassium chlorate and potassium chloride. K=39, Cl=35·5, O=16. [Ans. $KClO_3$=51·04% $KClO_4$=48·96%]

32. 6 grams of a mixture of potassium chlorate and potassium chloride, on being heated, give 1·9 gram of oxygen. Calculate the percentage of potassium chlorate in the mixture. K=39, Cl=35·5, O=16. [Ans. 80·8%]

33. Crude calcium carbide is made in an electric furnace by the following reaction : $CaO+3\,C \rightarrow CaC_2+CO$

The product contains 85% CaC_2 and 15% unreacted CaO. (a) How much of CaO is to be added to the furnace charge for each 1,000 kilograms of CaC_2 (pure) produced ? (b) How much CaO is to be added to the furnace charge for each 1,000 kilograms of crude product ? Ca=40, C=12, O=16 [Ans. (a) 1051·47 kg. of CaO ; (b) 893·75 kg. of CaO] [I. I. T., '67]

34. 10 grams of a mixture of $CaCO_3$ and CaO, on being heated, give 3·3 grams of carbon dioxide. Calculate the percentage of $CaCO_3$ in the mixture. Ca=40, O=16. [Ans. 75%]

35. A sample of aluminium contains some alumina (Al_2O_3) as impurities. When 2 grams of this sample react with hydrochloric acid, 0·2 gram of hydrogen are produced. Calculate the percentage of aluminium and alumina in the sample. (Al=27, Cl=35·5, H=1) [Ans. Al=90% Al_2O_3=10%]

36. Calculate the amount of sulphuric acid required to neutralise ammonia obtained by heating 10·7 gram of ammonium chloride with slaked lime (CaO). N=14, Cl=35·5, H=1 [Ans. 9·8 gram]

37. A sample of marble contains some silica as impurities. When 11 grams of this sample react with 10 grams of sulphuric acid, 0·2 gram of the acid remains unreacted. Calculate the percentage of $CaCO_3$ present in the sample of marble. Ca=40, C=12, O=16 [Ans. 90·91%]

38. When excess of silver nitrate solution is added to a solution containing 6 grams of common salt 14·35 grams of AgCl are precipitated. Calculate the percentage of NaCl in the common salt. Ag=108, Cl=35·5, Na=23 [Ans. 97·5%]

39. Calculate the ratio of the weights of potassium chlorate and hydrogen peroxide which will liberate the same weight of oxygen. K=39, Cl=35·5, H=1, O=16 [Ans. 1·2 : 1]

40. 1 gram of a mixture of calcium and magnessium require 2·19 grams of HCl for its complete dissolution. Calculate the amount of the two metals in the mixture. (Ca=40, Mg=24, Cl=35·5) [Ans. 0·7 grams and 0·3 grams]

41. When 50 grams of a mixture of anhydrous sodium carbonate and

sodium bicarbonate is heated 46·9 gram of a residue is obtained. Calculate the percentage of sodium carbonate in the mixture.
Na=23, H=1, C=12, O=16 [Ans. 83·2%]

42. 1·96 grams of H_2SO_4 is required for dissolving 1·56 gram of a mixture of $CaCO_3$ and CaO. What is the percentage of $CaCO_3$ in the mixture ?
Ca=40, C=12, S=32, H=1, O=16. [Ans. 64·1%]

(ii) Weight-volume problems. So far, only the weights of the substances which take part in the chemical reactions have been calculated. But it is often necessary to calculate the volume of a gas which will react or be produced in a chemical reaction when a given weight of a substance is used. The volume of the gas can be deduced from its weight since one gram-molecular weight of any gas at N. T. P. occupies 22·4 litres.

In this type of calculations, correct equations are to be written and the following relations are utilized :

(i) The reactions expressed by the equations are supposed to take place at N. T. P. (0°C and 760 mm. pressure).

(ii) The gas equation : $\frac{P_1V_1}{T_1}=\frac{P_2V_2}{T_2}$. where P_1, V_1, T_1 and P_2, V_2, T_2 are the pressure, volume and temperature of a gas under two sets of conditions.

(iii) One gram-molecule of any gas occupies 22·4 litres at N. T. P.

(iv) The weight of 1 litre of hydrogen at N. T. P. is 0·09 gram.

(v) The relative density of air (H=1) is 14·4.

(vi) The weight of 1 litre of air at N.T.P. is 1·295 gram.

(vii) Molecular weight$=2\times$vapour density.

(viii) The weight of 1 litre of a gas at N. T. P.=its vapour density$\times$0·09 gram.

(ix) Mass=Volume$\times$Density.

(x) Atomic weight=Equivalent weight$\times$valency.

(xi) Number of moles of a gas

$$=\frac{\text{Volume of the gas at N.T.P. (in litre)}}{22\cdot4 \text{ litre}}.$$

Ex. 1. What volume of oxygen is obtained at N. T. P. by heating 1 gram of potassium chlorate ?

$$\underset{245}{2KClO_3} = 2KCl + \underset{3\times22\cdot4 \text{ litres at N.T.P.}}{3O_2}$$

245 grams of $KClO_3$ yield $3\times22\cdot4$ litres of oxygen at N.T.P.

∴ 1 gram of $KClO_3$ yield $\frac{3\times22.4}{245}$ or, 0·2742 litre of oxygen at N.T.P.

∴ Volume of oxygen at N. T. P. is 274·2 c.c.

Ex. 2. A balloon of 1,000 litres capacity is to be filled with hydrogen at 27°C and 750 mm. Calculate the minimum quantity of iron required to liberate the necessary amount of hydrogen.

[C. U., '25]

Solution. Hydrogen can be prepared by the action of red-hot iron on steam or by the action of iron on cold dilute sulphuric acid.

$$\underset{3\times 55{\cdot}8 \text{ grams}}{3Fe} + 4H_2O = Fe_3O_4 + \underset{4\times 22{\cdot}4 \text{ litres at N. T. P.}}{4H_2} \quad \ldots \quad \ldots \quad \text{(i)}$$

$$\underset{55{\cdot}8 \text{ grams}}{Fe} + H_2SO_4 = FeSO_4 + \underset{22{\cdot}4 \text{ litres at N. T. P.}}{H_2} \quad \ldots \quad \ldots \quad \text{(ii)}$$

From (i), we see that 55·8 grams of iron liberate $\frac{4\times 22{\cdot}4}{3}$ litres of hydrogen at N. T. P. while equation (ii) reveals that 55·8 grams of iron liberate 22·4 litres of hydrogen at N. T. P. Hence, smaller amount of iron will be required in the steam-iron process.

Let 1,000 litres of hydrogen at 27°C and 750 mm. occupy V litres at N. T. P., then $\frac{1000\times 750}{(27+273)}=\frac{V\times 760}{273}$ or, V = 897·988 litres.

At N.T.P. 4 × 22·4 litres of hydrogen are obtained from 3 × 55·8 grams of iron

∴ 897·988 litres of hydrogen are obtained from

$\frac{3\times 55{\cdot}8\times 897{\cdot}988}{4\times 22{\cdot}4}$ or 1677·7 grams of iron.

∴ the minimum quantity of iron required is 1677·7 grams.

Ex. 3. Assuming that the oxygen content of air is 20 per cent by volume, calculate what volume of air at 27°C and 750 mm. pressure is required to burn completely 50 grams of a paraffin candle containing 80 per cent carbon and 20 per cent hydrogen.

Solution : 100 grams of candle contain 80 grams of carbon and 20 grams of hydrogen.

∴ 50 grams of candle contain $\frac{80\times 50}{100}$ or, 40 grams of carbon and $\frac{20\times 50}{100}$ or 10 grams of hydrogen.

$$\text{(i)} \quad \underset{12 \text{ grams}}{C} + \underset{22{\cdot}4 \text{ litres at N.T.P.}}{O_2} = CO_2$$

12 grams of carbon burn in 22·4 litres of oxygen (at N.T.P.)

∴ 40 grams of carbon burn in $\frac{22.4\times 40}{12}$ or 74·666 litres of oxygen (at N.T.P.)

$$\text{(ii)} \quad \underset{4 \text{ gms}}{2H_2} + \underset{22.4 \text{ litres at N. T. P.}}{O_2} = 2H_2O$$

4 grams of hydrogen burn in 22·4 litres of oxygen (at N.T.P.)

∴ 10 grams of hydrogen burn in $\frac{22{\cdot}4 \times 10}{4} = 56$ litres of oxygen at N. T. P.

Hence, 50 grams of candle burn in $(74{\cdot}666 + 56)$ or $130{\cdot}666$ litres of oxygen (at N.T.P.)

∴ the volume of air at N.T.P. $= \frac{100 \times 130{\cdot}666}{20}$ or $653{\cdot}33$ litres.

Let $653{\cdot}33$ litres of air at N.T.P. occupy V litres at 27°C and 750 mm. pressure. Then, $\frac{V \times 750}{(27+273)} = \frac{653{\cdot}33 \times 760}{273}$

or, $V = 727{\cdot}33$ litres.

Ex. 4. Hydrogen sulphide prepared by the action of dilute sulphuric acid on a sample of ferrous sulphide contained 10% of hydrogen by volume. Calculate the percentage of free iron in the sample of ferrous sulphide. $(Fe = 56, S = 32)$.

Solution : Let the percentage of free iron in the sample be x; then 100 grams of the sample contain $(100 - x)$ grams of FeS.

$$\text{(i)}\quad \underset{\text{88 grams}}{FeS} + H_2SO_4 = FeSO_4 + \underset{\text{22·4 litres at N.T.P.}}{H_2S}$$

$(100 - x)$ gram of FeS produce $\frac{22{\cdot}4 \times (100 - x)}{88}$ litres of H_2S (at N. T. P.)

$$\text{(ii)}\quad \underset{\text{56 grams}}{Fe} + H_2SO_4 = FeSO_4 + \underset{\text{22·4 litres at N.T.P.}}{H_2}$$

x grams of iron produce $\frac{22{\cdot}4 \times x}{56}$ litres of hydrogen at N.T.P.

The ratio of the volumes of H_2S and H_2 in the mixture is 90 : 10,

$$\frac{22{\cdot}4 \times (100 - x)}{88} : \frac{22{\cdot}4 \times x}{56} = 90 : 10 \quad \text{or} \quad x = 6{\cdot}6$$

Hence, the percentage of iron is 6·6.

Ex. 5. Hydrogen obtained by the action of sulphuric acid on 10 grams of zinc is passed over 50 grams of pure, dry cupric oxide. Calculate the weight of the residue and the volume of the gaseous product at 100°C and 76 cm. pressure $(Zn = 65 ; Cu = 63)$. [C.U., '19]

Solution : $\underset{65}{Zn} + H_2SO_4 = ZnSO_4 + \underset{\text{22·4 litres at N.T.P.}}{H_2}$

65 grams of zinc liberate 22·4 litres of H_2 at N.T.P.

∴ 10 grams of zinc liberate $\frac{22{\cdot}4 \times 10}{65}$ or $3{\cdot}446$ litres of H_2 at N. T. P.

Again, 65 grams of zinc liberate 2 grams of hydrogen

∴ 10 grams of zinc liberate $\frac{2\times10}{65}$ or 0·3077 gram of hydrogen

$$\underset{}{CuO} + \underset{22{\cdot}4\ \text{litres at N.T.P.}}{H_2} = Cu + \underset{22{\cdot}4\ \text{litres at N.T.P.}}{H_2O\ (\text{steam})}$$

22·4 litres of H_2 form 22·4 litres of steam at N.T.P.

∴ 3·446 litres of H_2 form 3·446 litres of steam at N.T.P.

Let this volume of steam at 100°C and 76 cm. Hg be V litres.

Then, $\frac{V\times760}{(100+273)}=\frac{3{\cdot}446\times760}{273}$ ∴ $V=4{\cdot}7158$ litres.

Now, 4 grams of hydrogen combine with 32 grams of oxygen

∴ 0·3077 grams of hydrogen combine with $\frac{32\times0{\cdot}3077}{4}$ or 2·4616 grams of oxygen.

Hence, 2·4616 grams of oxygen are derived from 50 grams of CuO.

The weight of the residue is, therefore, $(50-2{\cdot}4616)=47{\cdot}5384$ grams.

Ex. 6. Calculate the amount of $KClO_3$ which on complete decomposition will yield just sufficient oxygen required to burn 1113·6 litres of lighting gas containing 50 per cent of hydrogen, 35 per cent of methane, 8 per cent of carbon monoxide, 2 per cent of ethylene and 5 per cent of non-combustible admixtures at 27°C and 750 mm. pressure.

Solution : Let 1113·6 litres of lighting gas occupy V litres at N. T. P.

Then, $\frac{V\times760}{273}=\frac{1113{\cdot}6\times750}{27+273}$ or $V=1{,}000$ litres.

100 litres of the gas contain 50 litres of hydrogen

∴ 1000 liters of the gas contain $\frac{50\times1000}{100}$ or 500 litres of hydrogen.

∴ Volume of H_2 in the gas mixture = 500 litres.
Similarly, volume of CH_4 = 350 litres.
Volume of CO = 80 litres.
Volume of C_2H_4 = 20 litres.

(i) $$\underset{2\times22{\cdot}4\ \text{litres at N.T.P.}}{2H_2} + \underset{22{\cdot}4\ \text{litres at N.T.P.}}{O_2} = 2H_2O$$

2 × 22·4 litres of H_2 burn in 22·4 litres of O_2

∴ 500 litres of H_2 burn in 250 litres of O_2

(ii) $$\underset{22{\cdot}4\ \text{litres at N.T.P.}}{CH_4} + \underset{2\times22{\cdot}4\ \text{litres at N.T.P.}}{2O_2} = CO_2 + 2H_2O$$

22·4 litres of CH_4 burn in 2 × 22·4 litres of O_2 at N.T.P.

∴ 350 litres of CH_4 burn in 2 × 350 or 700 litres O_2 at N.T.P.

(iii) $2CO + O_2 = 2CO_2$
2 × 22·4 litres at N.T.P. 22·4 litres at N.T.P.

2 × 22·4 litres of CO burn in 22·4 litres of O_2 at N.T.P.
80 litres of CO burn in 40 litres of O_2 at N.T.P.

(iv) $C_2H_4 + 3O_2 = 2CO_2 + 2H_2O$
22·4 litres at N.T.P. 3 × 22·4 litres at N.T.P.

22·4 litres of C_2H_4 burn in 3 × 22·4 litres of O_2 at N.T.P.

∴ 20 litres of C_2H_4 burn in 60 litres of O_2 at N.T.P.

∴ Total volume of oxygen required = (250 + 700 + 40 + 60) or 1050 litres.

This volume of oxygen must be obtained by the decomposition of $KClO_3$.

$$\underset{245\text{ grams}}{2KClO_3} = 2KCl + \underset{3\times 22\cdot 4\text{ litres at N.T.P.}}{3O_2}$$

3 × 22·4 litres of O_2 are obtained from 245 grams of $KClO_3$

∴ 1050 liters of O_2 are obtained from $\frac{245\times 1050}{3\times 22\cdot 4}$ or 3827·95 grams of $KClO_3$.

Ex. 7. 1 gram of a mixture of the carbonates of calcium and magnesium gave 240 c.c. of carbon dioxide at N.T.P. Calculate the composition of the mixture. (Ca=40, Mg=24) [B. Sc. Manc.]

Solution : 22·4 litres of CO_2 weigh 44 grams at N.T.P.

∴ 0·24 litres of CO_2 weigh $\frac{44\times 0\cdot 24}{22\cdot 4}$ grams at N.T.P.

Let the weight of calcium carbonate in the mixture be x gram then the weight of magnesium carbonate is $(1-x)$ gram

$$\underset{100}{CaCO_3} = CaO + \underset{44}{CO_2}$$

100 grams of $CaCO_3$ produce 44 grams of CO_2

∴ x grams of $CaCO_3$ produce $\frac{44\times x}{100}$ grams of CO_2

$$\underset{84}{MgCO_3} = MgO + \underset{44}{CO_2}$$

84 grams of $MgCO_3$ produce 44 grams of CO_2

∴ $(1-x)$ grams of $MgCO_3$ produce $\frac{44\times(1-x)}{84}$ grams of CO_2

$\therefore \frac{44 \times x}{100} + \frac{44(1-x)}{84} = \frac{44 \times \cdot 24}{22 \cdot 4}$ or $x = \cdot 6242$

$\therefore$ Percentage of $CaCO_3$ = 62·42
Percentage of $MgCO_3$ = 37·58.

Ex. 8. On dissolution of 0·8 gram of zinc dust (zinc powder containing a small quantity of zinc oxide admixture) in dilute sulphuric acid, 252·8 ml. of moist hydrogen were liberated as measured at 767 mm pressure and 27 C. Calculate the percentage of zinc in zinc dust. (Aqueous tension at 27°C=27 mm).

Solution : Let the volume of hydrogen at N.T.P. be V c.c. ;

$$\text{Then, } \frac{760 \times V}{273} = \frac{252 \cdot 8 \times (767 - 27)}{(27 + 273)}$$

$\therefore$ V=224 c.c.

$$\underset{65 \text{ grams}}{Zn} + H_2SO_4 = ZnSO_4 + \underset{22 \cdot 4 \text{ litres at N.T.P.}}{H_2}$$

$\therefore$ 224 c.c. of hydrogen is obtained from $\frac{65 \times 0 \cdot 224}{22 \cdot 4} = 0 \cdot 65$ grams of zinc.

$\therefore$ 0·8 gram of zinc dust contain 0·65 gram of zinc.

$\therefore$ Percentage of zinc$= \frac{0 \cdot 65 \times 100}{0 \cdot 8} = 81 \cdot 25$.

Ex. 9. 224 c.c. of sulphur dioxide at N.T.P. just decolorises 200 c.c. of a solution of potassium permanganate in dilute sulphuric acid. Calculate the strength of potassium permanganate solution in grams per litre, (Mn=55).

Solution : Gram-molecular weight of SO_2=64 grams.

$\therefore$ 22·4 litres of SO_2 is the volume occupied by 64 grams of SO_2 at N.T.P.

$\therefore$ 0·224 litres of SO_2 is the volume occupied by $\frac{64 \times \cdot 224}{22 \cdot 4}$ or 0·64 gram of SO_2 at N.T.P.

$$\underset{316 \text{ grams}}{2KMnO_4} + \underset{320 \text{ grams}}{5SO_2} + 2H_2O = K_2SO_4 + 2MnSO_4 + 2H_2SO_4$$

320 grams of SO_2 decolorise 316 grams of $KMnO_4$

$\therefore$ 0·64 grams of SO_2 decolorise $\frac{316 \times 0 \cdot 64}{320} = 0 \cdot 632$ gram of $KMnO_4$.

$\therefore$ Amount of $KMnO_4$ in grams/litre=3·16 grams.

Ex. 10. When 2·45 grams of potassium chlorate were strongly heated, 672 c.c. of oxygen were envolved at N.T.P. and the residue left was 1·49 grams. Calculate the density of oxygen and its molecular weight.

Solution : Weight of oxygen $=2{\cdot}45-1{\cdot}49=0{\cdot}96$ grams.

Now, 672 c.c. of oxygen at N.T.P. weigh 0·96 gram.

$\therefore$ 1,000 c.c. of oxygen at N.T.P. weigh $\frac{0{\cdot}96\times1{,}000}{672}$ or 1·43 gram.

$\therefore$ 22·4 litres of oxygen at N.T.P. weigh $1{\cdot}43\times22{\cdot}4$ or 32 grams.

$\therefore$ Density of oxygen is 1·43 gram/litre and molecular weight is 32.

Ex. 11. $Ca(OH)_2+2NH_4Cl=CaCl_2+2NH_3+2H_2O$

From the above equation, calculate the amount of NH_4Cl required to prepare 2·024 litres of NH_3 at 750 mm. pressure and 0°C. What will be the amount of $CaCl_2$ produced ? Ca=40.

[H. S., '81]

Let the volume of NH_3 produced at N.T.P. be V litres.

Then, $\frac{V\times760}{273}=\frac{2{\cdot}024\times750}{273}$ $\therefore$ $V=1{\cdot}9973$ litres.

$$\underset{}{Ca(OH)_2}+\underset{2\times53\cdot5}{2NH_4Cl}=\underset{111}{CaCl_2}+\underset{2\times22\cdot4\text{ litres (at N.T.P.)}}{2NH_3}$$

At N.T.P. $2\times22{\cdot}4$ litres of NH_3 are obtained from $2\times53{\cdot}5$ gram of NH_4Cl.

$\therefore$ At N.T.P. 1·9973 litres of NH_3 are obtained from $\frac{2\times53{\cdot}5\times1{\cdot}9973}{2\times22{\cdot}4}$, or 4·77 gram of NH_4Cl.

Again, $2\times53{\cdot}5$ gram of NH_4Cl give 111 gram of $CaCl_2$

$\therefore$ 4·77 gram of NH_4Cl give $\frac{111\times4{\cdot}77}{2\times53{\cdot}5}$ or 4·948 gram of $CaCl_2$.

$\therefore$ Weight of $NH_4Cl=4{\cdot}77$ gram and weight of $CaCl_2=4{\cdot}948$ gram.

Ex. 12. Calculate (i) the weight of MnO_2 and (ii) the volume of hydrochloric acid of specific gravity 1·12 and containing 40 per cent HCl by weight, needed to produce 1·78 litres chlorine gas at N.T.P. according to the reaction :

$$MnO_2+4HCl=MnCl_2+2H_2O+Cl_2$$

(Mn=54·9, H=1, Cl=35·5, O=16) [I. I. T., '77]

MnO_2 reacts with hydrochloric acid according to the equation :

$$\underset{(54\cdot9+32)}{MnO_2}+\underset{4\times36\cdot5}{4HCl}=MnCl_2+2H_2O+\underset{22\cdot4\text{ litres}}{Cl_2}$$

At N. T. P. 22·4 litres $Cl_2\equiv4\times36{\cdot}5$ gram of HCl

$\equiv86{\cdot}9$ gram of MnO_2

$\therefore$ At N. T. P. 1·78 litres $Cl_2\equiv11{\cdot}61$ gram HCl $\equiv6{\cdot}905$ gram MnO_2.

$\therefore$ The weight of HCl needed $= 11{\cdot}61$ gram

The weight of MnO_2 needed $= 6{\cdot}905$ gram

Now, 40 gram of HCl is present in 100 gram of the solution.

$\therefore$ 11·61 gram of HCl is present in $\frac{100 \times 11{\cdot}61}{40}$ or 29 gram of the solution.

$\therefore$ The required volume of HCl solution $= \frac{29}{1{\cdot}12} = 25{\cdot}9$ c.c.

Ex. 13. 5 grams of copper and 5 grams of sulphur are separately heated with excess of conc. H_2SO_4. Calculate the ratio of the volumes of SO_2 obtained in the two cases. (Cu=63, S=32)

$$\underset{63}{Cu} + 2H_2SO_4 = CuSO_4 + 2H_2O + \underset{22{\cdot}4 \text{ litres (at N.T.P.)}}{SO_2}$$

$$\underset{32}{S} + 2H_2SO_4 = 2H_2O + \underset{3 \times 22{\cdot}4 \text{ litres (at N.T.P.)}}{3SO_2}$$

At N.T.P., 63 grams of copper liberate 22·4 litres of SO_2

$\therefore$ At N.T.P., 5 grams of copper liberate $\frac{22{\cdot}4 \times 5}{63}$ litres of SO_2.

Again, 32 grams of sulphur liberate $3 \times 22{\cdot}4$ litres of SO_2 (at N.T.P.)

$\therefore$ 5 grams of sulphur liberate $\frac{3 \times 22{\cdot}4 \times 5}{32}$ litres of SO_2 (at N.T.P.)

$$\therefore \frac{\text{Volume of } SO_2 \text{ liberated by Cu}}{\text{Volume of } SO_2 \text{ liberated by S}} = \frac{22{\cdot}4 \times 5 \times 32}{63 \times 3 \times 22{\cdot}4 \times 5} = \frac{32}{189}$$

Hence, the ratio of the volumes of SO_2 obtained in the two case is 32 : 189.

Ex. 14. • What amount of zinc are dissolved in excess of dil sulphuric acid to liberate 0·57 litre of hydrogen at 27°C and 750 mm pressure ? What amount of zinc sulphate will be formed ?
(Zn=65, H=1) [H. S., '61]

Let the volume of hydrogen be V litres at N.T.P.

Then, $\frac{760 \times V}{273} = \frac{0{\cdot}57 \times 750}{(27+273)}$ $\therefore$ $V = \frac{0{\cdot}57 \times 750 \times 273}{760 \times 300}$

$\therefore$ $V = 0{\cdot}511$ litre.

$$\underset{65}{Zn} + H_2SO_4 = \underset{161}{ZnSO_4} + \underset{22{\cdot}4 \text{ litres at N.T.P.}}{H_2}$$

At N.T.P., 22·4 litres of hydrogen are obtained from 65 grams of Zn

$\therefore$ 0·511 litres of hydrogen are obtained from $\frac{65 \times 0{\cdot}511}{22{\cdot}4}$ or 1·482 grams of Zn.

∴ Required weight of Zn = 1·482 gram

Again, 65 grams of Zn produce 161 grams of $ZnSO_4$

∴ 1·482 grams of Zn produce $\frac{161 \times 1{\cdot}482}{65}$ or 3·671 gram of $ZnSO_4$.

∴ Weight of $ZnSO_4$ formed = 3·671 grams.

Ex. 15. Air contains 23% by weight of oxygen. Calculate the volume of air at 750 mm pressure and 27°C required to burn completely 30 grams of wax containing 80% carbon and 20% hydrogen.

Vapour density of air (H = 1) = 14·4 and the weight of 1 litre of hydrogen at N.T.P. = 0·09 gram.

30 grams of wax contain $\frac{80 \times 30}{100}$ or 24 grams of carbon and $\frac{20 \times 30}{100}$ or 6 grams of hydrogen.

(i) $\underset{12}{C} + \underset{32}{O_2} = CO_2$

12 grams of carbon are burnt in 32 grams of O_2

∴ 24 grams of carbon are burnt in $\frac{32 \times 24}{12}$ or 64 grams of oxygen.

(ii) $\underset{4}{2H_2} + \underset{32}{O_2} = 2H_2O$

4 grams of hydrogen are burnt in 32 grams of O_2

∴ 6 grams of hydrogen are burnt in $\frac{32 \times 6}{4} = 48$ grams of O_2.

Hence, in order to burn 30 grams of wax (64 + 48) or 112 grams of oxygen are required.

Now, 23 grams of oxygen are present in 100 grams of air.

∴ 112 grams of oxygen are present in $\frac{100 \times 112}{23}$ or 487 grams of air.

At N.T.P. the weight of 1 litre of hydrogen = 0·09 gram

∴ At N.T.P. the weight of 1 litre of air = 14·4 × ·09 = 1·296 gram.

At N.T.P. the volume of 1·296 gram of air = 1 litre

∴ At N.T.P. the volume of 487 grams of air = $\frac{1 \times 487}{1{\cdot}296}$ or 375·77 litres.

Let the volume of the air at 27°C and 750 mm pressure be V_2 litre.

$$\text{Then, } \frac{V_2 \times 750}{(273+27)} = \frac{375{\cdot}77 \times 760}{273}$$

$$\therefore \quad V_2 = \frac{375{\cdot}77 \times 760 \times 300}{273 \times 750} = 418{\cdot}4 \text{ litres.}$$

Ex. 16. A 1·00 gram sample of $KClO_3$ was heated under such conditions that a part of it decomposed according to the equation.

(i) $2KClO_3 = 2KCl + 3O_2$

and the remaining underwent change according to the equation

(ii) $4KClO_3 = 3KClO_4 + KCl$

If the amount of oxygen evolved was 146·8 ml at S. T. P., calculate the percentage by weight of $KClO_4$ in the residue.

[I. I. T., '77]

$$\text{(i)} \quad \underset{2\times122{\cdot}5}{2KClO_3} \quad = \quad \underset{2\times74{\cdot}5}{2KCl} \quad + \quad \underset{3\times22400 \text{ c.c. at N.T.P.}}{3O_2}$$

$$\text{At N.T.P. } 3\times22400 \text{ c.c. O} \equiv 2\times122{\cdot}5 \text{ gram } KClO_3$$
$$\equiv 2\times74{\cdot}5 \text{ gram } KCl$$

$$\therefore \quad 146{\cdot}8 \text{ c.c. } O_2 \equiv \frac{2\times122{\cdot}5\times146{\cdot}8}{3\times22400} \text{ gram } KClO_3$$
$$\equiv \frac{2\times74{\cdot}5\times146{\cdot}8}{3\times22400} \text{ grams of } KCl.$$

$$\therefore \quad 146{\cdot}8 \text{ c.c. } O_2 \equiv 0{\cdot}5352 \text{ gram } KClO_3 \equiv 0{\cdot}3255 \text{ gram } KCl$$

Hence, 146·8 c.c. of O_2 are evolved by the decomposition of 0·5352 gram of $KClO_3$ and 0·3255 grams of KCl are left as residue.

∴ Remaining (1 – 0·5352) or 0·4648 gram of $KClO_3$ decompose according to the equation :

$$\underset{4\times122{\cdot}5}{4KClO_3} \quad = \quad \underset{3\times138{\cdot}5}{3KClO_4} \quad + \quad \underset{74{\cdot}5}{KCl}$$

$4\times122{\cdot}5$ gram $KClO_3 \equiv 3\times138{\cdot}5$ gram $KClO_4 \equiv 74{\cdot}5$ gram KCl

$$\therefore \quad 0{\cdot}4648 \text{ gram } KClO_3 \equiv \frac{3\times138{\cdot}5\times0{\cdot}4648}{4\times122{\cdot}5} \text{ gram } KClO_4$$
$$\equiv \frac{74{\cdot}5\times0{\cdot}4648}{4\times122{\cdot}5} \text{ gram KCl}$$

∴ 0·4648 gram of $KClO_3 \equiv 0{\cdot}3941$ gram $KClO_4 \equiv 0{\cdot}07067$ gram KCl.

$$\therefore \quad \text{Total weight of residue} = 0{\cdot}3941 + 0{\cdot}07067 + 0{\cdot}3255$$
$$= 0{\cdot}79027 \text{ gram.}$$

$$\therefore \quad \%\ KClO_4 \text{ in the residue} = \frac{0{\cdot}3941\times100}{0{\cdot}79027} = 49{\cdot}86$$

Problems

1. How many litres of acetylene will be produced at N.T.P. when 8 grams of calcium carbide react with water ? [Ans. 2·8 litres]

2. What weight of water will be produced by passing 10 litres of hydrogen measured at 760 mm and 0°C over 1·00 gram of heated copper oxide ? (Cu = 64) [Ans. 0·225 grams]

3. What volume of oxygen at 12°C and 780 mm will be required to burn all the hydrogen evoled by the action of dilute HCl on 25 grams of zinc ? Zn = 65·4 [C. U., '08]

4. When burned, 3 grams of anthracite liberated 5·3 litres of carbon dioxide measured at N. T. P. What was the carbon content of the anthracite ? [Ans. 94·66%]

5. What weight of potassium chlorate is required to liberate 1 litre of oxygen at N. T. P. ? [Ans. 3·645 grams]

6. What weight of calcium carbonate is required to prepare 5·6 litres of carbon dioxide at N. T. P. ? [Ans. 25 grams]

7. Assuming that oxygen content of air is 20 per cent by weight calculate the weight of sulphur required to convert all the oxygen in 1000 litres of air at 27°C and 760 mm pressure into sulphur dioxide. [Ans. 235·872 grams]

[Hints : Let 1000 litres of air under this condition occupy V litres at N.T.P. $\therefore \frac{V \times 760}{273} = \frac{1000 \times 760}{300}$ or V = 910 litres. Now, one litre of any gas at N. T. P. weighs 0·09 × d grams where d is the density of the particular gas referred to hydrogen as unity. ∴ the weight of 910 litres of air at N. T. P = 910 × 14·4 × ·09 or 1179·36 grams. Again, 1179·36 grams of air contain $\frac{20 \times 1179 \cdot 36}{100}$ or 235·872 grams of oxygen and hence, etc.]

8. What volume of air at 27°C and 750 mm would be required for the complete combustion of 100 volumes of gaseous mixture containing 46% H_2, 40% CH_4 and 14% CO by volume ? Air may be assumed to contain 21% O_2 by volume. [Ans. 536·7 vols.] [C. U., '21.]

9. Assuming that oxygen content of air is 20 per cent by volume, calculate what volume of air is required to burn one cubic metre of technical water gas containing 50 per cent of hydrogen, 40 per cent of carbon monoxide, 5 per cent of carbon dioxide and 5 per cent of nitrogen. [Ans. 2·25 cu. m.]

10. Assuming that air contains 20 per cent by weight of oxygen, calculate the volume of air at 27°C and 750 mm pressure that would be required for complete combustion of one kilogram of coal, containing 81% C, and 9% hydrogen. [Ans. 12373·2 litres]

[**Hints** : 1 kg. of coal contains 810 grams of carbon and 90 grams of hydrogen. 810 grams of carbon require $\frac{32 \times 810}{12}$ or 2160 grams of O_2 and 90 grams of H_2 require $\frac{32 \times 90}{4} = 720$ grams of O_2 ∴ Total amount of O_2 required = (2160 + 720) or 2880 grams, Now 2880 grams of O_2 are present in $\frac{100 \times 2880}{20}$ or 14400 grams of air. Again weight of 1 litre of air at N. T. P. = 14·4 × 0·09 or 1·296 gram.

∴ 1·296 gram of air occupy 1 litre at N. T. P.

∴ 14400 grams of air occupy $\frac{14400}{1 \cdot 296}$ or 11111 litres at N.T.P. Let this volume of air at N.T.P. occupy V litre at 27°C and 750 mm pressure. $\therefore \frac{11111 \times 760}{273} = \frac{V \times 750}{300}$ or V = 12373·2 litres.]

11. Calculate the amount of $KClO_3$ which on complete decomposition will yield oxygen just sufficient for the complete combustion of 1099 c.c. of a gas mixture containing 20 per cent acetylene and 80 per cent carbon monoxide at 27°C and 760 mm pressure. [Ans. 3·2811 grams]

12. A balloon of 1000 litres capacity is to be filled with hydrogen at 27°C and 760 mm pressure. Calculate the amount of iron required to liberate necessary amount of hydrogen.

[Ans. 1706·25 grams by steam-iron method and 2275 grams by the action of acids.]

13. 1·3158 grams of a sample of limestone was dissolved in HCl in air-free apparatus. The volume of the gas (free from acid vapour and moisture) measured at 27°C and 750 mm pressure was found to be 311·8 c.c. On strongly heating, 1·0526 grams of the same sample left a residue of 0·6126 gram. What is the density of the gas at N. T. P. and its molecular weight ?

[Ans. 44 ; 0·001964 g/c.c.] [C. U., '40]

[Hints : Let the volume of 311·8 c.c. of the gas at 27° and 750 mm pressure be V c.c. at N. T. P. $\therefore \frac{311\cdot8\times750}{300}=\frac{V\times760}{273}$ or V = 280 c.c.

Now, 1·3158 grams of the sample evolve 280 c.c. of the gas at N. T. P.

$\therefore$ 1·0526 grams of the sample evolve $\frac{280\times1\cdot0526}{1\cdot3158}$ or 224 c.c. of the gas at N. T. P.

Now, 1·0526 grams of limestone on strongly heating liberate 224 c.c. of the gas at N. T. P. and then leave a residue of 0·6126 gram. $\therefore$ 224 c.c. of the gas weigh (1·0526 − 0·6126) grams or ·44 gram at N. T. P. $\therefore$ 22·4 litres of the gas weigh 44 grams at N. T. P. Now, density of the gas is 0·44/224 or 0·001964 gram/c.c.

14. Calculate the amount of granulated zinc which would liberate 1000 c.c. of dry hydrogen at 30°C and 754 mm pressure, assuming that zinc completely reacts with dilute sulphuric acid. (Zn = 65) [Ans. 2·600 gram] [C. U., '55]

15. Exactly 3 grams of magnesium carbonate ($MgCO_3$) were added to 5·00 grams of dilute sulphuric acid ; after all action had ceased, it was found that 0·480 gram was left undissolved. Calculate the percentage strength of sulphuric acid.

In this reaction what volume of carbon dioxide would be evolved measured at N. T. P. ? (Mg = 24) [Ans. 58·96%, 670 c.c.]

16. A blackened silver spoon weighing 50 grams on treatment with hydrochloric acid evolves 100 c.c. of H_2S at 27°C and 760 mm pressure. Calculate the percentage of silver in silver spoon. [Ans. 97·868%]

17. Calculate the volume of hydrogen at 27°C and 750 mm pressure that would be produced by the decomposition of 3·6 grams of water (i) by sodium and (ii) by calcium hydride. [Ans. (i) 2·494 litres, (ii) 4·988 litres]

18. A sample of dolomite contains 50% $CaCO_3$, 40% $MgCO_3$ and 10% clay. Calculate the volume of CO_2 measured at 27°C and 750 mm pressure which would be evolved on heating 10 grams of the sample with HCl.

[Ans. 2·434 litres]

19. How many litres of carbon dioxide at N. T. P. should be passed through a solution of calcium hydroxide, $Ca(OH)_2$ to obtain 25 grams of $CaCO_3$.

[Ans. 5·6 litres]

20. 10 c.c. of a solution of hydrogen peroxide liberated 0·254 gram of iodine from KI solution. Calculate the strength of hydrogen peroxide solution in terms of (a) gram per litre and (b) "volume" strength.

[Ans. (a) 3·4 grams/litre (b) 11·2 vol.]

[Hints : $\underset{34}{H_2O_2}+2HCl+2KI=2KCl+2H_2O+\underset{254}{I_2}$

0·254 gram of iodine is liberated by $\frac{34\times0{\cdot}254}{254}=0{\cdot}034$ gram of H_2O_2.

∴ Amount of $H_2O_2=\frac{0{\cdot}034\times1000}{10}$ or 3·4 grams per litre and the solution is 0·34 per cent strong. (b) Now, 1% solution of hydrogen peroxide is of "3·3" volume strength. ∴ 0·34% solution of hydrogen peroxide is of 3·3 × 0·34 or 1·122 volume strength.]

21. 0·5 gram of a sample of chalk containing silica on treatment with hydrochloric acid liberated 100 c.c. of CO_2 measured at 27°C and 750 mm pressure. Find the percentage of silica in the sample. [Ans. 20%]

22. Calculate the volume of air at 27°C and 760 mm pressure that will be required for the complete combustion of 1 gram of a sample of pyrite containing 60% of sulphur assuming that air contains 20 per cent of oxygen by volume. [Ans. 2·307 litres]

23. 20 grams of copper and sulphur are separately heated with excess of concentrated sulphuric acid. Compare the volumes of sulphur dioxide produced. [Ans. 32 : 189]

24. What volume of gas ought to be obtained by the solution of 76·2 grams of copper in strong sulphuric acid, the gas being measured at 21°C and 791 mm ? [Ans. 27·5 litre] [London Inter.]

25. The air in a room was tested for carbon dioxide by drawing 100 litres of it at 27°C and 750 mm. pressure through caustic potash. The increase in weight of the potash was 1·5 gram. Calculate the percentage by weight of CO_2 in the air of the room. [Ans. 1·28%]

26. 1 gram of a compound contains 0·075 gram hydrogen, 0·262 gram nitrogen and 0·663 gram chlorine. Calculate the weight of the compound required to obtain 1 litre of ammonia gas at 27°C and 760 mm pressure. [Ans. 2·173 gram] [H. S. (Comp.), '62]

27. A sample of zinc contains zinc oxide as impurities. When 1 gram of the sample of zinc is dissolved in dil. HCl 130 c.c. of dry hydrogen is obtained at 50°C and 755 mm pressure. Calculate the percentage of zinc in the sample. Zn = 65 [Ans. 31·65%] [London Matric]

28. When 0·1 gram of a mixture of aluminium and magnesium is dissolved in dil. HCl 220 c.c. of dry hydrogen is obtained at 27°C and 760 mm pressure. Calculate the percentage composition of the mixture. Al = 27, Mg = 24 [Ans. Al = 34·266% Mg = 65·734%]

29. 2 grams of a mixture of $NaHCO_3$ and Na_2CO_3 contain the two constituents in equal amounts. Calculate the volume of carbon dioxide evolved at N. T. P. when 2 grams of the mixture is heated until a constant weight is obtained. [Ans. 133·33 c.c.]

30. A sample of aluminium contains alumina as impurities. When 0·032 gram of the sample is dissolved in dil. HCl 39·3 c.c. of hydrogen is obtained at 13°C and 761 mm pressure. Calculate the amount of impurities in per cent in the sample. Aqueous tension at 13°C = 11 mm Hg. [Ans. 7·47%] [Cal., '46]

31. 1 gram of iron is converted into ferric chloride. What volume of H_2S at N. T. P. will reduce the aqueous solution of this ferric chloride into ferrous chloride ? Fe = 56. [Ans. 200 c.c.] [Patna, '23]

32. A sample of potassium chlorate contains potassium chloride as impurities. Oxygen evolved when 1·555 gram of this sample is decomposed burns completely 152 c.c. of acetylene at 27°C and 750 mm pressure. Calculate the percentage of $KClO_3$ in the sample. [Ans. 80·13%] [Cal., '40]

33. The density of a dilute sulphuric acid is 1·55 gram./c.c. and it contains

65% by weight of H_2SO_4. What volume of hydrogen at 27°C and 750 mm pressure will be evolved when 750 grams of zinc react with 1 litre of this acid? (Zn = 65) [Ans. 256·43 litre] [H. S. '75]

34. What weight of pure calcium carbonate will be required to prepare 1 litre of CO_2 at 27°C and standard pressure? What weight of pure carbon will be required to prepare this amount of CO_2? [Ans. 4·062 gram, 0·4874 gram] [Cal., '29]

35. The density of a dil. HCl is 1·2 gram/c.c. and it contains 50% by weight of HCl. Calculate the volume of this acid required to react completely with 7·9 gram of cupric oxide. (Cu = 63) [Ans. 12·167 c.c.]

(iii) Volume-volume problems. Eudiometry. When two or more gases take place in a chemical reaction, it is possible to calculate the volume of one gas which will react with or be produced from a known volume of another gas. The solution to such problems is provided by the direct inspection of a balanced chemical equation. Thus the equation $2CO + O_2 = 2CO_2$ indicates that 2 gram-molecules of carbon monoxide react with 1 gram-molecule of oxygen to form 2 gram-molecules of carbon dioxide. Since one gram-molecule of any gas occupies 22·4 litres at N.T.P., we can say that 2 × 22·4 litres of carbon monoxide react with 22·4 litres of oxygen to form 2 × 22·4 litres of carbon dioxide at N.T.P. If one gram-molecule of any gas is supposed to occupy one volume, then we can make the statement that under the same conditions of temperature and pressure 2 volumes of carbon monoxide react with one volume of oxygen to produce 2 volumes of carbon dioxide. One volume then becomes equal to 22·4 litres at N.T.P. The following reactions will serve as illustrations :

(i)	$2H_2$	+	O_2	=	$2H_2O$	(steam)
	2 vol.		1 vol.		2 vol.	contraction=1 vol.
(ii)	$2H_2$	+	O_2	=	$2H_2O$	(liquid)
	2 vol.		1 vol.		0 vol.	contraction=3 vol.
(iii)	C	+	O_2	=	CO_2	
	(solid)		1 vol.		1 vol.	contraction=nil
(iv)	CH_4	+	$2O_2$	=	CO_2	+ $2H_2O$ (liquid)
	1 vol.		2 vol.		1 vol.	0 vol. contraction=2 vol.
(v)	$2NH_3$			=	N_2	+ $3H_2$
	2 vol.				1 vol.	3 vol. expansion=2 vol.
(vi)	NH_3	+	HCl	=	NH_4Cl	(solid)
	1 vol.		1 vol.		0 vol.	contraction=2 vols.
(vii)	N_2	+	O_2	=	2NO	
	1 vol.		1 vol.		2 vol.	contraction=nil

Since the volume occupied by a liquid or a solid is negligible in comparison with the volume of a gas, a solid or a liquid is assumed to occupy zero volume in gas analysis.

Determination of the formula of a pure gas. The formula of gases can be calculated by the application of Gay-Lussac's law of volumes to the volume relationships of the reacting substances and their products. The method can be explained by the reaction between chlorine and excess of ammonia solution. From the experiment, it is found that 3 volumes of chlorine displace from an unknown volume of ammonia, 1 volume of nitrogen. Now, 3 volumes of chlorine react with 3 volumes of hydrogen. Hence nitrogen and hydrogen are present in ammonia in the ratio of

$$\frac{\text{1 volume of nitrogen}}{\text{3 volumes of hydrogen}}$$

$$\text{or, } \frac{\text{1 molecule of nitrogen}}{\text{3 molecules of hydrogen}} \quad \text{(by Avogadro's hypothesis)}$$

$$\text{or, } \frac{\text{2 atoms of nitrogen}}{\text{6 atoms of hydrogen}} \quad \text{(since nitrogen and hydrogen molecules are diatomic.)}$$

$$\text{or, } \frac{\text{1 atom of nitrogen}}{\text{3 atoms of hydrogen}}$$

Hence the formula of ammonia is NH_3 or N_2H_6 or some other multiple of NH_3. Determination of vapour density of the gas supports the formula NH_3.

Determination of the formula of a gaseous hydrocarbon. The formula of a gaseous hydrocarbon can be determined by exploding it with a measured excess of oxygen. After cooling the mixture to the original temperature, the contraction due to explosion is noted. The carbon dioxide formed is then absorbed in caustic potash and its amount is thus found. The contraction that occurs due to the removal of carbon dioxide is then noted. To illustrate the method of calculation, the following example may be taken. Let the hydrocarbon C_mH_n be exploded in known excess of oxygen, m and n being the number of atoms of carbon and hydrogen respectively.

Let the volume of hydrocarbon taken $= V_1$ c.c.
the contraction on explosion $= V_2$ c.c.
the volume of carbon dioxide produced $= V_3$ c.c.

Now, each molecule of the hydrocarbon, when exploded with excess oxygen, yields m molecules of carbon dioxide and n/2 molecules of water. Since one molecule of carbon dioxide contains 2 atoms of oxygen and one molecule of water contains 1 atom of oxygen, the total number of oxygen atoms required for complete combustion of one molecule of hydrocarbon is $\left(2m+\frac{n}{2}\right)$. Since the oxygen molecule is diatomic, the number of oxygen molecules required for the complete combustion of one molecule of hydrocarbon is $\left(m+\frac{n}{4}\right)$.

Hence the reaction which occurs on explosion may be represented by the following equation :

$$C_mH_n+\left(m+\frac{n}{4}\right)O_2=mCO_2+\frac{n}{2}H_2O$$

1 volume of C_mH_n reacts with $\left(m+\frac{n}{4}\right)$ volume of oxygen to form m volumes of carbon dioxide ; the reaction is accompanied by a contraction in volume. Hence V_1 c.c. of C_mH_n react with $V_1\times\left(m+\frac{n}{4}\right)$ c.c. of oxygen to form mV_1 c.c. of carbon dioxide.

$\therefore$ volume before explosion$=V_1+V_1\left(m+\frac{n}{4}\right)+$ unreacted oxygen and volume after explosion$=mV_1+$unreacted oxygen.

$\therefore$ contraction on explosion$=V_1+V_1\left(m+\frac{n}{4}\right)-mV_1=V_2$

$\therefore\ V_1+\frac{n}{4}V_1=V_2 \qquad \therefore\ n=4\left(\frac{V_2}{V_1}-1\right)$

Now, volume of carbon dioxide$=mV_1$

$$\therefore\ mV_1=V_3 \qquad \therefore\ m=\frac{V_3}{V_1}$$

V_1, V_2 and V_3 are found out by experiment and hence the value of *m* and *n* can be determined. The formula of the hydrocarbon can, therefore, be deduced.

Problems

Ex. 1. 5 c.c. of a gaseous hydrocarbon were mixed with an excess of oxygen and the mixture exploded by means of an electric spark. The contraction observed was 10 c.c. On adding a concentrated solution of potassium hydroxide, there is a further contraction of 10 c.c. ; the residual gas being pure oxygen. Calculate the formula of the hydrocarbon gas.

Solution : Let the formula of the gaseous hydrocarbon be $CmHn$ where *m* and *n* are respectively the number of carbon and hydrogen atoms. Then its reaction with oxygen is represented by

$$CmHn+\left(m+\frac{n}{4}\right)O_2=mCO_2+\frac{n}{2}H_2O$$

$\therefore$ 5 c.c. of $CmHn+5\times\left(m+\frac{n}{4}\right)$ c.c. of O_2

$=5m$ c.c. of CO_2+contraction

$\therefore$ Contraction$=5+5\left(m+\frac{n}{4}\right)-5m=10$

$\therefore \ \frac{n}{4}=1 \qquad \therefore \ n=4$

Volume of $CO_2=5m=10$. $\quad \therefore \ m=2$

$\therefore$ The formula of hydrocarbon is C_2H_4.

Ex. 2. 100 volumes of a mixture of carbon monoxide and acetylene were mixed with 250 volumes of oxygen in an eudiometer and fired. After cooling, the residual gases occupied 260 volumes, and after treatment with potash the residual oxygen occupied 120 volumes. What was the composition of the mixture ?

Solution : Let x volume of acetylene be present in the mixture, then the volume of carbon monoxide$=(100-x)$.

The reactions which take place, when exploded with oxygen, are

$$\begin{array}{llllll} \text{(i)} & C_2H_2 & + \ \frac{5}{2}O_2 & = & 2CO_2 & + \ H_2O \\ & 1 \text{ vol.} & \frac{5}{2} \text{ vol.} & & 2 \text{ vols.} & \\ & x \text{ vols.} & \frac{5}{2}\,x \text{ vols.} & & 2x \text{ vols.} & \\ \text{(ii)} & CO & + \ \frac{1}{2}O_2 & = & CO_2 & \\ & 1 \text{ vol.} & \frac{1}{2} \text{ vol.} & & 1 \text{ vol.} & \\ & (100-x) \text{ vol} & \frac{1}{2}(100-x) \text{ vol} & & (100-x) \text{ vol.} & \end{array}$$

volume of $CO_2=2x+(100-x)=260-120=140$

$\therefore \ x=40$.

Hence, the composition of the mixture is : acetylene, 40 vols. and carbon monoxide, 60 vols.

Ex. 3. 25 c.c. of a mixture of gases consisting of nitrogen and nitric oxide is passed over ignited metallic copper and the resulting product collected and was found to occupy 20 c.c. Calculate the percentage composition of the original mixture, the gases being measured at the same temperature and pressure. [C. U., '20]

Solution : Let the volume of nitric oxide be x c.c. Then the volume of nitrogen is $(25-x)$ c.c. The reaction which occurs is

$$\begin{array}{ll} NO \ + \ Cu=CuO+\frac{1}{2}N_2 \\ 1 \text{ vol.} \qquad\qquad\qquad \frac{1}{2} \text{ vol.} \end{array}$$

$\therefore$ x c.c. of nitric oxide on reduction yield $\frac{x}{2}$ c.c. of nitrogen.

$\therefore$ volume of nitrogen$=\frac{x}{2}+(25-x)=20$ or $x=10$ c.c.

$\therefore$ percentage of nitric oxide$=\frac{10\times100}{25}=40$

$\therefore$ percentage of nitrogen$=\frac{15\times100}{25}=60$.

Ex. 4. A mixture containing 40 c.c. of nitrous oxide and 40 c.c. of nitric oxide was exploded with 80 c.c. of hydrogen. All the hydrogen was used up and no unreacted nitrous oxide and nitric oxide remained. The volume of nitrogen produced was found to be 60 c.c. Determine the formula of nitric oxide if that of nitrous oxide be N_2O.

Solution : The reaction of nitrous oxide with hydrogen is represented as,

$$\underset{1\text{ vol.}}{N_2O} + \underset{1\text{ vol.}}{H_2} = \underset{1\text{ vol.}}{N_2} + H_2O$$

∴ 40 c.c. of nitrous oxide react with 40 c.c. of hydrogen to produce 40 c.c. of nitrogen.

∴ Nitrogen formed from nitric oxide$=60-40=20$ c.c.

Now, 40 c.c. of hydrogen has reacted with nitrous oxide and hence the volume of hydrogen which reacted with nitric oxide$=(80-40)=40$ c.c. But 40 c.c. of hydrogen react with 20 c.c. of oxygen.

Hence, 40 c.c. of nitric oxide contain 20 c.c. of nitrogen and 20 c.c. of oxygen.

or, 1 c.c. of nitric oxide contain $\frac{1}{2}$ c.c. of nitrogen and $\frac{1}{2}$ c.c. of oxygen.

or, 1 molecule of nitric oxide contains $\frac{1}{2}$ molecule, i.e., 1 atom of nitrogen and $\frac{1}{2}$ molecule, i.e., 1 atom of oxygen.

Hence, molecular formula of nitric oxide is NO.

Ex. 5. On passing through strongly heated charcoal one litre of a gas mixture of CO and CO_2 is found to give 1600 c.c. of CO both measured under the same conditions. Calculate the composition of the mixture.

[C. U., '14]

Solution. Let x c.c. be the volume of CO_2 in the mixture.

∴ volume of CO$=(1000-x)$ c.c.

The reaction that takes place is : $C + \underset{1\text{ vol.}}{CO_2} = \underset{2\text{ vols.}}{2CO}$

Hence, x c.c. of CO_2 produce $2x$ c.c. of CO. The volume of CO produced from the mixture of CO_2 and CO$=2x+(1000-x)=1600$

∴ $x=600$

∴ volume of $CO_2=600$ c.c. and volume of CO$=400$ c.c.

Ex. 6. 100 c.c. of oxygen were subjected to silent electric discharge and the volume of the ozonised oxygen was found to be 70 c.c. What was the percentage of ozone in the ozonised oxygen ?

Solution. Let the volume of ozone in the ozonised oxygen be x c.c. ∴ The volume of oxygen$=70-x$ c c. Oxygen is ozonised according to the following equation :

$$\underset{3\text{ vol.}}{3O_2} \rightleftharpoons \underset{2\text{ vol.}}{2O_3}$$

$\therefore$ 2 c c. of ozone is formed from 3 c.c. of oxygen.

$\therefore$ x c.c. of ozone is formed from $\frac{3x}{2}$ c.c. of oxygen

$\therefore$ $\frac{3x}{2}+70-x=100$ or $x=60$

$\therefore$ percentage of ozone in the ozonised oxygen$=\frac{60\times 100}{70}$ or 85·71.

Ex. 7. For the purpose of determining the formula of a gaseous hydrocarbon, its 5 c.c. were mixed with 12 c.c. of oxygen and the mixture was exploded in an eudiometer. On condensation of the water vapour, the volume of the gaseous residue was 7 c.c. and after treatment with alkali, it reduced to 2 c.c. All measurements were made in the same conditions. Calculate the formula of the hydrocarbon.

Solution. Let the formula of the hydrocarbon be CmHn where *m* and *n* are the number of carbon and hydrogen atoms respectively. The reaction which takes place is

$$C_mH_n+\left(m+\frac{n}{4}\right)O_2 \quad = \quad mCO_2+\frac{n}{2}H_2O$$

$$1 \text{ vol.} \quad \left(m+\frac{n}{4}\right)\text{vol.} \qquad m \text{ vol.}$$

$\therefore$ 1 c.c. of C_mH_n give m c.c. of carbon dioxide.

5 c.c. of C_mH_n give $5m$ c c. of carbon dioxide

$\therefore$ volume of carbon dioxide$=5m$ c.c.$=(7-2)$ or 5 c.c.

$\therefore$ $m=1$.

Now, 5 c.c. of C_mH_n react with $5\left(m+\frac{n}{4}\right)$ c.c. of O_2

Volume of oxygen reacted$=12-2=10$ c.c.

$\therefore$ $5\left(m+\frac{n}{4}\right)=10$

$\therefore$ $5\left(1+\frac{n}{4}\right)=10$ $\qquad\therefore$ $n=4$.

Hence, the formula of hydrocarbon is CH_4.

Ex. 8. One volume of a gaseous compound containing carbon, hydrogen and oxygen was burnt in the presence of 2·5 volumes of oxygen. On complete combustion the resultant gases contained 2 volumes of steam and two volumes of carbon dioxide. All volumes were measured under identical conditions. What is the formula of the compound? [I. I. T., '66]

Solution. Let the formula of the compound be $C_xH_yO_z$. The equation for the combustion is :

$$C_xH_yO_z + xO_2 + \frac{y}{4}O_2 - \frac{z}{2}O_2 = xCO_2 + \frac{y}{2}H_2O$$

$$1\text{ vol.} \quad x\text{ vol.} \quad \frac{y}{4}\text{ vol.} \quad \frac{z}{2}\text{ vol.} \quad x\text{ vol} \quad \frac{y}{2}\text{ vol.}$$

volume of CO_2 produced=2 vols.=x vol.

$$\therefore\ x=2$$

Volume of steam produced=2 vols.=$\frac{y}{2}$ vol.

$$\therefore\ y=4$$

Again, volume of reacted oxygen=2·5 vol.

$$\therefore\ x+\frac{y}{4}-\frac{z}{2}=2\cdot5 \qquad \therefore\ z=1.$$

Hence, the formula of the compound is C_2H_4O.

Ex. 9. Ten ml of a gaseous organic compound containing C, H and O only, was mixed with 100 ml of oxygen and exploded under conditions which allowed the water formed to condense. The volume of the gas after explosion was 90 ml. On treatment with potash solution a further contraction in volume of 20 ml. was observed. Given that the vapour density of the compound is 23, deduce the molecular formula. All volume measurements were carried out under the same conditions. [I. I. T., '77]

Solution. Let the formula of the organic compound be $C_xH_yO_z$. It burns in oxygen according to the following equation :

$$C_xH_yO_z + xO_2 + \frac{y}{4}O_2 - \frac{z}{2}O_2 = xCO_2 + \frac{y}{2}H_2O$$

$$1\text{ vol.} \quad x\text{ vol.} \quad \frac{y}{4}\text{ vol.} \quad \frac{z}{2}\text{ vol.} \quad x\text{ vol.} \quad \text{'0' vol.}$$

$$10\text{ c.c.} \quad 10x\text{ c.c.} \quad \frac{10y}{4}\text{ c.c.} \quad \frac{10z}{2}\text{ c.c.} \quad 10x\text{ c.c.}$$

$$\text{First contraction}=10+10x+\frac{10y}{4}-\frac{10z}{2}-10x$$

$$=110-90=20$$

$$\therefore\ 10+\frac{10y}{4}-\frac{10z}{2}=20$$

$$\therefore\ \frac{10y}{4}-5z=10 \qquad \text{(i)}$$

volume of CO_2 formed=$10x=20$

$$\therefore\ x=2$$

Hence the formula of the compound is $C_2H_yO_z$

$\therefore$ Its molecular weight $=2\times12+y\times1+z\times16$

The vapour density of the compound $=23$

$\therefore$ Its molecular weight $=23\times2=46$

$\therefore$ $2\times12+y\times1+z\times16=46$

or, $24+y+16z=46$

or, $y+16z=22$ (ii)

From equations (i) and (ii) we get

$z=1$ and $y=6$

$\therefore$ The molecular formula of the compound is C_2H_6O.

Ex. 10. 0·9 gram of a solid organic compound (molecular weight 90) containing carbon, hydrogen and oxygen was heated with oxygen corresponding to a volume of 224 ml at S.T.P. After combustion the total volume of the gases was 560 ml at S.T.P. On treatment with potassium hydroxide, the volume decreased to 112 ml. Determine the molecular formula of the compound.

[I. I. T., '72]

Solution. Number of moles of organic compound taken $=\frac{0{\cdot}9}{90}=0{\cdot}01$

At S.T.P. the volume of CO_2 produced $=560-112=448$ c.c.

$\therefore$ number of moles of CO_2 produced $=\frac{448}{22400}=0{\cdot}02$

The volume of oxygen that has reacted $=224-112=112$ c.c. at N.T.P.

number of moles of oxygen that has reacted $=\frac{112}{22400}=0{\cdot}005$

Let the formula of the organic compound be $C_xH_yO_z$. It burns in oxygen according to the following equation :

$$C_xH_yO_z \;+\; \left(x+\frac{y}{4}-\frac{z}{2}\right)O_2 = xCO_2 \;+\; \frac{y}{2}H_2O$$

0·01 mole	0·005 mole	0·02 mole
1 mole	0·5 mole	2 mole

$\therefore$ $x=2$ (i)

$x+\frac{y}{4}-\frac{z}{2}=0{\cdot}5$

or, $2+\frac{y}{4}-\frac{z}{2}=0{\cdot}5$ or $\frac{y}{4}-\frac{z}{2}=-1{\cdot}5$ (ii)

Again, $12x+1\times y+16\times z=90$

or, $12\times2+y+16z=90$

or, $y+16z=66$ (iii)

From equation (ii) we get, $y-2z=-6$

From equation (iii) we get, $y+16z=66$

$\therefore\ 18z=72 \qquad \therefore\ z=4$

$\therefore\ y=2$

$\therefore$ The formula of the organic compound is $C_2H_2O_4$.

Ex. 11. 60 ml of a mixture of equal volumes of chlorine and an oxide of chlorine was heated and then cooled back to the original temperature. The resulting gas mixture was found to have a volume of 75 ml. On treatment with caustic soda solution the volume contracted to 15 ml. Assuming that all measurements were made at the same temperature and pressure, deduce the simplest formula of the oxide of chlorine. (The oxide of chlorine on heating decomposes quantitatively to oxygen and chlorine.) [I. I. T., '71]

Solution. Let the formula of the oxide of chlorine be Cl_mO_n.

Volume of Cl_2 before heating=30 ml.

Volume of Cl_mO_n before heating=30 ml.

Contraction of volume by NaOH solution=75 – 15=60 c.c.

Volume of Cl_2 in the mixture after the reaction=60 c.c.

$\therefore$ Volume of oxygen=15 c.c.

Volume of Cl_2 produced in the reaction=60 – 30=30 c.c.

Chlorine oxide decomposes according to the following equation :

$$\begin{array}{lcl}
Cl_mO_n = & \frac{m}{n}Cl_2 + & \frac{n}{2}O_2 \\
1 \text{ vol.} & \frac{m}{2} \text{ vol.} & \frac{n}{2} \text{ vol.} \\
30 \text{ c.c.} & 30 \text{ c.c.} & 15 \text{ c.c.} \\
1 \text{ c.c.} & 1 \text{ c.c.} & \frac{1}{2} \text{ c.c.}
\end{array}$$

$$\therefore\ \frac{m}{2}=1 \qquad \therefore\ m=2$$

$$\frac{n}{2}=\frac{1}{2} \qquad \therefore\ n=1$$

$\therefore$ The formula of chlorine oxide=Cl_2O.

EXERCISES

1. 20 c.c. of a hydrocarbon were exploded with 250 c.c. of air. The immediate contraction was 40 c.c. and the volume of CO_2 found by KOH absorption was 20 c.c. What is the composition of the hydrocarbon ?

[Ans. CH_4] [C. U., '32]

2. 10 c.c. of a gaseous hydrocarbon were exploded with excess of O_2. The contraction observed was 15 c.c. On treatment with KOH a further contraction of 20 c.c. took place. What is the molecular formula of the hydrocarbon ? [Ans. C_2H_2]

3. 25 c.c. of marsh gas at N. T. P. are mixed with 300 c.c. of air at 27°C and 750 mm pressure and the mixture is exploded by electric sparks. Find out the volume of the residual gas at 17°C and 750 mm. Air contains 20% O_2 and 80% N_2 by volume. [Ans. 263·09 c.c.] [C. U., '16]

4. To a mixture of acetylene, hydrogen and carbon monoxide occupying 20 c.c., 50 c.c. of oxygen were added and a spark passed. After cooling, the residual gases contained 16 c.c. of carbon dioxide and 36 c. c. of unburnt oxygen. What was the composition of the mixture ?

[Ans. 2 c.c. C_2H_2, 6 c.c. H_2 and 12 c.c. CO]

[**Hints :** Let x c.c. be the volume of acetylene, y c.c. be the volume of hydrogen ; then volume of CO $=(20-x-y)$ c.c. The reactions occurring are :

$$\text{(i)}\quad \begin{array}{lll} C_2H_2+\frac{5}{2}O_2 & = & 2CO_2+H_2O \\ x\text{ c.c.}\ \ \frac{5}{2}x\text{ c.c.} & & 2x\text{ c.c.} \end{array}$$

$$\text{(ii)}\quad \begin{array}{ll} H_2+\frac{1}{2}O_2 & =H_2O \\ y\text{ c.c.}\ \frac{1}{2}y\text{ c.c.} & \end{array} \qquad \text{(iii)}\quad \begin{array}{ccccc} CO & + & \frac{1}{2}O_2 & = & CO_2 \\ (20-x-y) & & \frac{1}{2}(20-x-y) & & (20-x-y) \end{array}$$

Now, volume of carbon dioxide produced $=2x+(20-x-y)=16$ or $x-y=-4$

Volume of oxygen reacted $=\frac{5}{2}x+\frac{1}{2}y+\frac{1}{2}(20-x-y)=50-36$ or 14 c.c.

$$\therefore\ 4x=8 \quad \therefore\ x=2 \quad \therefore\ y=6.$$

$\therefore$ Volume of acetylene $=2$ c.c., volume of hydrogen $=6$ c.c. and volume of carbon monoxide $=12$ c.c.]

5. Calculate from the following data the composition of nitrous oxide :

Volume of gas taken $=10$ c.c. ; volume after addition of hydrogen $=28$ c.c. ; volume after explosion $=18$ c.c. ; volume after addition of oxygen $=27$ c.c. and volume after second explosion $=15$ c.c. [C. U., '19]

(The volumes are reduced to N. T. P.)

6. 50 c.c. of a mixture of CO and C_2H_2 gases were mixed with 100 c.c. of oxygen in an eudiometer and fired. After cooling the residual gases occupied 100 c.c. and after treatment with potash the residual gases occupied 50 c.c. Calculate the composition of the original mixture.

[Ans. CO 80 % and C_2H_2 20%]

7. A mixture of oxygen and carbon monoxide is exposed to the action of ultraviolet light. Ozone and carbon dioxide are the new gases formed in the reaction. If 100 c.c. of gas were taken in which the ratio O_2/CO was 1·015, how many c.c. of each of the gases will be found in the residue which measures 85·87 c.c. and has the ratio $CO_2/CO=0{\cdot}2419$?

[**Hints.** Let the volume of oxygen present in 100 c.c. of the gas-mixture be x c.c. then the volume of CO is $(100-x)$ c.c.

$$\therefore\ \frac{x}{100-x}=1{\cdot}015 \text{ or } x=50{\cdot}37$$

$\therefore$ volume of oxygen $=50{\cdot}37$ c.c. and volume of CO $=49{\cdot}63$ c.c.

Let V_1 and V_2 be the volumes of O_2 and CO which are converted into O_3 and CO_2 respectively. The reactions taking place are :

$$\begin{array}{lllll} \text{(i)} & 3O_2 & \rightleftharpoons\ 2O_3 & & \text{contraction} \\ & 3\text{ vols.} & 2\text{ vols.} & & 1\text{ vol.} \\ \textit{i.e.,} & 1\text{ vol.} & \frac{2}{3}\text{ vol.} & & \frac{1}{3}\text{ vol.} \\ & V_1\text{ c.c.} & \frac{2}{3}V_1\text{ c.c.} & & \frac{1}{3}V_1\text{ c.c.} \end{array}$$

$$\begin{array}{llllll} \text{(ii)} & CO & +\ \frac{1}{2}O_2 & = & CO_2 & \text{contraction} \\ & 1\text{ vol.} & \frac{1}{2}\text{ vol.} & & 1\text{ vol.} & \frac{1}{2}\text{ vol.} \\ & V_2\text{ c.c.} & \frac{1}{2}V_2\text{ c.c.} & & V_2\text{ c.c.} & \frac{1}{2}V_2\text{ c.c.} \end{array}$$

$\therefore$ Total contraction $= (\frac{1}{3}V_1 + \frac{1}{2}V_2)$ c.c. $= 100 - 85{\cdot}87 = 14{\cdot}13$ c.c.

or, $2V_1 + 3V_2 = 84{\cdot}78$

Now, $\dfrac{\text{vol. of CO}_2\text{ produced}}{\text{vol. of CO left unreacted}} = \dfrac{V_2}{(49{\cdot}63 - V_2)} = 0{\cdot}2419$

or, $V_2 = 9{\cdot}6626$

Again $2V_1 + 3V_2 = 84{\cdot}78$

or, $2V_1 + 3 \times 9{\cdot}6626 = 84{\cdot}78$ or, $V_1 = 27{\cdot}8961$.

$\therefore$ volume of ozone present in the residue $= \frac{2}{3}V_1 = \frac{2}{3} \times 27{\cdot}8961$ or $18{\cdot}5974$ c.c.

volume of CO_2 present in the residue $= V_2$ c.c. $= 9{\cdot}6626$ c.c.

volume of oxygen present in the residue

$= 50{\cdot}37 -$ (volume of oxygen used up)

$= 50{\cdot}37 - (v_1 + \frac{1}{2}V_2) = 50{\cdot}37 - (27{\cdot}8961 + 4{\cdot}8313)$

$= 17{\cdot}6426$ c.c.

and volume of $CO = 49{\cdot}63 - V_2 = 49{\cdot}63 - 9{\cdot}6626 = 39{\cdot}968$ c.c.

Total volume of the residue $= 85{\cdot}8706$ c.c.

8. 10 c.c. of a hydrocarbon were mixed with 50 c.c. of oxygen in an eudiometer and fired. The volume of the residual gas was 40 c.c. and on adding caustic potash the volume decreased to 20 c.c. What was the hydrocarbon ?
[Ans. C_2H_4]

9. 100 c.c. of a mixture of nitrous oxide and nitric oxide were mixed with equal volume of hydrogen in an eudiometer and fired. The residue consisting of pure nitrogen was found to be 60 c.c. Calculate the composition of the mixture.
[Ans. N_2O, 20 c.c. & NO, 80 c.c.]

10. 100 c.c. of a mixture of CO, CH_4 and H_2 are mixed with 300 c.c. of O_2 in an eudiometer and fired. After cooling the resulting gas occupied 285 c.c. and after absorption by potash 205 c.c. of O_2 remained. Find the composition of the mixture. [Ans. CH_4, 30 c.c. ; CO, 50 c.c. and H_2, 20 c.c.,] [C. U., '41]

11. A mixture of carbon monoxide, methane and ethane measuring 10 c.c. was mixed with 40 c.c. of oxygen and fired in a moist eudiometer. After cooling the residual gases were found to consist of 12 c.c. of carbon dioxide and 23 c.c. of unconsumed oxygen. What was the composition of the mixture ?
[Ans. CO, 4 c.c. ; CH_4 4 c.c. ; C_2H_6 2 c.c.]

12. 100 c.c. of a sample of coal gas containing 40% H_2, 30% CH_4, 20% CO and 10% C_2H_2 were exploded with 1 litre of air in an eudiometer. Assuming that air contains 20 per cent oxygen, calculate the composition of the residual gas.
[Ans. CO_2 7·33% ; O_2 8·9% N_2 83·76%]

13. 10 c.c. of ethylene are mixed with 50 c.c. of oxygen in an eudiometer and fired. If the measurements are made above 100°C, what is the composition of the products ? [Ans. CO_2, 33·33% ; O_2, 33·33% steam, 33·33%]

14. 60 c.c. of oxygen is subjected to silent electric discharge and the volume of ozonised oxygen becomes 50 c.c. Calculate the composition of ozonised oxygen. [Ans. O_3, 20 c.c. O_2, 30 c.c.]

15. 70 c.c. of oxygen was partly ozonised and the decrease in volume was 5 c.c. Calculate the volume of ozone produced. If the resulting gas is treated with excess of potassium iodide solution, then what weight of iodine would be liberated ? [Ans. 10 c.c. O_3, 0·1134 grams of I_2]

16. 25 c.c. of oxygen is required for the complete burning of 10 c.c. of a mixture of methane and ethylene. What is the composition of each gas by volume ? [Ans. CH_4 50% C_2H_4 50%]

17. On passing 100 c.c. of nitrogen dioxide over heated copper 50 c.c. of nitrogen is obtained under the same conditions of temperature and pressure.

The vapour density of the compound is 23 at 140°C. What is the molecular formula of the compound ? [Ans. NO_2]

18. 10 c.c. of nitric oxide were heated with a spiral of iron by electric current. The remaining gas after cooling was found to occupy 5 c.c. Deduce the molecular formula of nitric oxide, 100 c.c. of the gas weighing 0·1339 gram at N. T. P. [Ans. NO]

19. 60 c.c. of a mixture of chlorine monoxide and chlorine dioxide were decomposed by heating and the chlorine produced were absorbed in KOH solution. As a result there is a decrease in volume of 50 c.c. Determine the composition of the mixture of the oxides. [Ans. Cl_2O, 40 c.c. ClO_2 20 c.c.]

20. On passing 100 c.c. of ozonised oxygen through a red-hot tube 120 c.c. of the gas is obtained. Calculate the percentage composition by volume of the original mixture. [Ans. O_3, 40% O_2 60%]

21. Ten ml. of a gaseous hydrocarbon was burnt completely in 80 ml. of oxygen at N.T.P. The remaining gas occupied 70 ml. at N.T.P. This volume became 50 ml. on treatment with KOH solution. What is the empirical formula of the hydrocarbon ? [Ans. CH_2] [I. I. T., '76]

22. A gaseous organic compound (A) is mixed with a volume of oxygen which is just sufficient to burn it completely. After burning 9 volumes of this mixture it is found that 4 volumes of CO_2, 6 volumes of steam and 2 volumes of nitrogen are formed under the same conditions of temperature and pressure. If the organic compound contains only carbon, hydrogen and nitrogen, then what volume of oxygen is required to burn it completely ? What is the molecular formula of the compound (A) ? [Ans. 7 volumes ; $C_2H_6N_2$]

23. 12 c.c. of a gaseous hydrocarbon is mixed with excess of oxygen and the mixture is exploded. After explosion the contraction in volume was 30 c.c. After shaking the mixture with KOH solution. a further contraction of 24 c.c. was observed. Calculate the molecular formula of the gas.

[Ans. C_2H_6] [J. E. E., '74]

24. 20 c.c. of a gaseous hydrocarbon was mixed with 66 c.c. of oxygen and the mixture was exploded. After explosion the volume of the residual gases in the cold condition was found to be 56 c.c. After shaking this mixture with KOH solution, the volume of the mixture further reduced to 16 c.c. The gas which is left is oxygen. Determine the molecular formula of the hydrocarbon.

[Ans. C_2H_2] [J. E. E., '73]

25. 100 c.c. of a mixture of carbon monoxide, methane and hydrogen was mixed with 300 c.c. of oxygen and the mixture was exploded. After cooling the volume of the resultant gas was 285 c.c. After treatment with KOH solution, 205 c.c. of oxygen was left. Determine the composition of the gaseous mixture.

[Ans. CO, 50 c.c. ; CH_4, 30 c.c. ; and H_2, 20 c.c.] [J. E. E., '71]

CHAPTER VI

CHEMICAL EQUIVALENTS

6.1. Introduction. A study of the proportions by weight in which various elements combine led to the introduction of a very important concept—the concept of equivalent weight. Let us consider, for example, two hydrogen compounds, viz., hydrogen chloride and sodium hydride.

In hydrogen chloride, 35·457 grams of chlorine combine with 1·008 grams of hydrogen.

In sodium hydride, 23 grams of sodium combine with 1·008 grams of hydrogen.

Now, the weights of sodium and chlorine which combine with a fixed weight of hydrogen in these compounds (e.g., 1·008 parts by weight) are 23 parts by weight and 35·457 parts by weight respectively and their ratio is 23 : 35·457. Also, 23 parts by weight of sodium combine with 35·457 parts by weight of chlorine to form sodium chloride. Thus, the weights of sodium and chlorine which separately combine with 1·008 parts by weight of hydrogen are also the weights in which sodium and chlorine combine with each other. Thus, 23 and 35·457 are the numbers which represent the weights in which sodium and chlorine combine with each other.

Similarly, *for all elements definite numbers can be found expressing the weights in which they combine with one another. These numbers are called the equivalent weights or combining weights or chemical equivalents.*

6.2. Standard on which equivalent weights are based. In order to calculate the equivalent weight of an element, it is necessary to select a fixed weight of some one element as a standard. At present, the standard is taken as 8 parts by weight of oxygen, i.e., the weight of an element which combines with 8 parts by weight of oxygen is taken as the equivalent weight of that element.

Dalton, in 1808, selected 1 part by weight of hydrogen as the standard. Since hydrogen is the lightest element, there will be the wide inequality of the weights to be measured. Again, there are many elements with which hydrogen does not form stable compoudns. On the other hand, almost all the elements except a few inert gases form compounds with oxygen which are generally very stable. Hence, the standard of equivalents was changed to oxygen as the standard, the equivalent weight of oxygen being taken equal to eight. On this basis, the accurate equivalent weight of hydrogen becomes 1·008.

The equivalent weight of an element is the weight of that element which will combine with or will displace from a compound, 8 parts by weight of oxygen (or, 1·008 parts by weight of hydrogen or 35·46 parts by weight of chlorine).

Equivalent weight of an element

$$=\frac{\text{Weight of the element}\times 8}{\text{Weight of combined or displaced oxygen}}$$

$$=\frac{\text{Weight of the element}\times 1\cdot 008}{\text{Weight of combined or displaced hydrogen}}$$

$$=\frac{\text{Weight of the element}\times 35\cdot 46}{\text{Weight of combined or displaced chlorine}}.$$

The equivalent weight is a number. When the equivalent weight of an element is expressed in grams, it is known as the *gram-equivalent weight of that element*.

Illustrations. (i) In water, H_2O, we find that 2·016 parts by weight of hydrogen combine with 16 parts by weight of oxygen. Or, 1·008 parts by weight of hydrogen combine with 8 parts by weight of oxygen. Hence, the equivalent weight of hydrogen is 1·008. Hydrogen and oxygen combine in water in the ratio 1·008 : 8, i.e., the ratio of their equivalent weights.

(ii) In hydrogen chloride, HCl, 1·008 parts by weight of hydrogen combine with 35·46 parts by weight of chlorine. Hence, the equivalent weight of chlorine is 35·46 and hydrogen and chlorine combine in the ratio of their equivalent weights, i.e., 1·008 : 35·46.

(iii) In sodium oxide, Na_2O, 46 parts by weight of sodium combine with 16 parts by weight of oxygen. Or, 23 parts by weight of sodium combine with 8 parts by weight of oxygen. Hence, 23 is the equivalent weight of sodium. Here also sodium and oxygen combine in the ratio of their equivalent weights, i.e., 23 : 8.

(iv) In calcium chloride, $CaCl_2$, 40 parts by weight of calcium combine with 70·92 parts by weight of chlorine. Or, 20 parts by weight of calcium combine with 35·46 parts by weight of chlorine. Hence, 20 is the equivalent weight of calcium and the ratio in which calcium and chlorine combine is 20 : 35·46.

(v) In the reaction, $Zn + H_2SO_4 = ZnSO_4 + H_2$, we find that 65·38 parts by weight of zinc displace 2·016 parts by weight of hydrogen from the compound, H_2SO_4. Or, 32·69 parts by weight of zinc displace 1·008 parts by weight of hydrogen. Hence, 32·69 is the equivalent weight of zinc.

From above examples, it is clear that the introduction of the concept, "equivalent weight", makes it possible to formulate the following law called the law of equivalent weights.

Elements combine with one another in the ratio of either their equivalent weights or simple multiples of their equivalent weights.

Law of reciprocal proportions and the Law of equivalent weights. In sodium oxide, Na_2O the ratio by weight of sodium and oxygen is $2\times23 : 16=23 : 8$. In sulphur dioxide, SO_2 the ratio by weight of sulphur and oxygen is $32 : 32=8 : 8$. Hence, according to the law of reciprocal proportions sodium and sulphur will combine in the ratio of $23 : 8$ or in the ratio of simple multiples of these numbers. In sodium sulphide, Na_2S we find that the ratio by weight of sodium and sulphur is $2\times23 : 32$ or $2\times23 : 4\times8$; 23 and 8 are respectively the equivalent weights of sodium and sulphur. Hence, the law of reciprocal proportions is another form of the law of equivalent weights or the law of equivalent proportions.

Let us suppose that A and B are two elements. a grams of A combine with 8 grams of oxygen and b grams of B combine with 8 grams of oxygen. By definition of equivalent weights, a and b are respectively the equivalent weights of A and B. According to the law of reciprocal proportions, when A and B combine with one another, their weight-ratio is $ma : nb$; $m=1, 2, 3$ etc. and $n=1, 2, 3$ etc. According to the law of equivalent proportions, when A and B combine with one another their weight-ratio is also $ma : nb$. Hence, the law of reciprocal proportions and the law of equivalent proportions are different forms of the same law.

6.3. Equivalent weight of an element may vary. Although each element possesses one atomic weight and one molecular weight, most elements possess more than one equivalent weight. This phenomenon arises due to the fact that *the same elements often combine in different proportions to form several different compounds.* The equivalent weights of such elements will obviously have different values. But in all such cases, the various equivalent weights of the same element are in proportion of small whole numbers. For example, iron reacts with oxygen to form either ferrous oxide, FeO or ferric oxide, Fe_2O_3. Now, in ferrous oxide, 27·925 parts by weight of iron combine with 8 parts by weight of oxygen. Again, in ferric oxide 18·616 parts by weight of iron combine with 8 parts by weight of oxygen. Hence, iron has two equivalent weights 27·925 and 18·616. Phosphorus may react with chlorine to give either phosphorus trichloride, PCl_3 or phosphorus pentachloride, PCl_5. The equivalent weight of chlorine is 35·46. In PCl_3, $31{\cdot}02/3=10{\cdot}34$ parts by weiht of phosphorus combine with 35·46 parts by weight of chlorine and in PCl_5 $31{\cdot}02/5=6{\cdot}20$ parts by weight of phosphorus combine with 35·46 parts by weight of chlorine. Therefore, phosphorus has two equivalent weights, 10·34 and 6·20.

In the following table are given examples of some elements whose equivalent weights vary.

Table 6·1

Compound	Weight-ratio	Equivalent weight of
Cuprous oxide Cu_2O	Cu : O = 63·5 : 8	Cu = 63·5
Cupric oxide, CuO	Cu : O = 37·75 : 8	Cu = 31·75
Carbon monoxide, CO	C : O = 6 : 8	C = 6·00
Carbon dioxide, CO_2	C : O = 3 : 8	C = 3·00
Stannous chloride, $SnCl_2$	Sn : Cl = 59·35 : 35·5	Sn = 59·35
Stannic chloride, $SnCl_4$	Sn : Cl = 29·675 : 35·5	Sn = 29·675

It will be shown later that the equivalent weights of an element are related to its valencies. Since *the valency of many elements varies, their equivalent weights vary.*

6.4. The equivalent weight of a radical. The equivalent weight of a radical may be defined as the number of parts by weight of it which will combine with 8·00 parts by weight of oxygen (or 1·008 parts by weight of hydrogen or 35·46 parts by weight of chlorine or its equivalent).

Illustrations. (i) In sulphuric acid, H_2SO_4, 48 parts by weight of sulphate radical SO_4^{--} combine with 1·008 parts by weight of hydrogen. Therefore, the equivalent weight of sulphate radical is 48.

(ii) In ammonium chloride, NH_4Cl, 18 parts by weight of ammonium radical, NH_4^+ combine with 35·46 parts by weight of chlorine. Hence, the equivalent weight of ammonium radical, NH_4^+, is 18.

(iii) In sodium carbonate, Na_2CO_3, 46 parts by weight of sodium combine with 60 parts by weight of the carbonate radical, CO_3^{--}. Or, 23 parts by weight of sodium combine with 30 parts by weight of the carbonate radical. Since the equivalent weight of sodium is 23, the equivalent weight of the carbonate radical becomes 30.

6.5. Equivalent weight of a compound. The conception of equivalent weights has been extended also to compounds.

The equivalent weight of a compound is the weight of the compound which will react without residue with 1·008 parts by weight of hydrogen or 8·00 parts by weight of oxygen (i.e., one equivalent weight of hydrogen or oxygen) or in general with one equivalent weight of any substance.

Let us consider the following examples :

(i) $\underset{2\cdot016}{H_2} + \underset{79\cdot57}{CuO} = H_2O + Cu$

When hydrogen is passed over strongly heated cupric oxide, 2·016 grams of hydrogen reduce 79·57 grams of cupric oxide or 1·008 grams of hydrogen reduce 39·78 grams of cupric oxide, CuO. Hence, the equivalent weight of cupric oxide is 39·78.

(ii) Mercuric sulphide reacts with oxygen according to the following equation :

$$\underset{232\cdot67}{HgS} + \underset{32}{O_2} = Hg + SO_2$$

In this reaction, 232·67 parts by weight of mercuric sulphide combine with 32 parts by weight of oxygen. Or, 8 parts by weight of oxygen combine with 58·17 parts by weight of mercuric sulphide. Therefore, the equivalent weight of mercuric sulphide is 58·17.

(iii) $\underset{24\cdot32}{Mg} + \underset{98}{H_2SO_4} = MgSO_4 + H_2$

24·32 parts by weight of magnesium react with 98 parts by weight of sulphuric acid or 49 parts by weight of sulphuric acid react with one equivalent weight of magnesium, i.e., 12·16 parts by weight. Hence, the equivalent weight of sulphuric acid is 49.

The equivalent weight of a compound can be calculated by adding the equivalent weights of its constituent elements or radicals. The calculation is shown in the examples given in table 6·2.

Table 6·2

Compound	Equivalent weights of the constituents	Equivalent weight of the compound
Magnesium chloride, $MgCl_2$	Mg = 12·16, Cl = 35·46	47·62
Calcium oxide, CaO	Ca = 20, O = 8	28
Sodium hydride, NaH	Na = 23, H = 1·008	24·008
Silver nitrate, $AgNO_3$	Ag = 107·88, NO_3^- = 62	169·88
Potassium chlorate, $KClO_3$	K = 39·096, ClO_3^- = 83·46	122·556
Magnesium sulphate, $MgSO_4$	Mg = 12·16, SO_4^{--} = 48	60·16

6·6. The relation among atomic weight, equivalent weight, and valency. The atomic weight, equivalent weight and valency of an element are related in a simple manner. The atomic weight of an element equals its equivalent weight multiplied by its valency :

Atomic weight = equivalent weight × valency.

Proof. Let us suppose that the atomic weight of an element $= x$
the equivalet weight of the element $= y$
and the valency of the element $= n$

Then by the definition of valency,

n atoms of hydrogen combine with 1 atom of the element. Hence, $n \times 1{\cdot}008$ parts by weight of hydrogen combine with $1 \times x$ parts by weight of the element. Or, 1·008 parts by weight of hydrogen combine with $\frac{x}{n}$ parts by weight of the element. Hence, by definition of the equivalent weight, we get, the equivalent weight of the element $= \frac{x}{n}$ or, $y = \frac{x}{n}$ or, $x = y \times n$

i.e., atomic weight = equivalent weight × valency.

Alternative proof. Let us suppose that
atomic weight of the element, $M = x$
equivalent weight of the element, $M = y$
and its velency $= n$

Hence, the formula of its oxide is M_2O_n

$\therefore$ Molecular weight of the oxide $= 2 \times x + n \times 16$

$\therefore$ $n \times 16$ grams of oxygen combine with $2x$ grams of the element.

$\therefore$ 8 grams of oxygen combine with $\frac{x}{n}$ grams of the element.

By definition of equivalent weight,

$$y = \frac{x}{n} \qquad \therefore \; x = y \times n$$

Hence, atomic weight = equivalent weight × valency.

Illustrations. (i) 12·16 parts by weight of magnesium replace 1·008 parts by weight of hydrogen from hydrochloric acid. Hence, equivalent weight of Mg = 12·16. Again, one atom of magnesium combines with one atom of oxygen to form magnesium oxide, MgO. One atom of oxygen combines with two atoms of hydrogen. Hence, the valency of magnesium is 2

Again, atomic weight of magnesium is 24·32

$$\therefore \text{ Valency of magnesium} = 2 = \frac{24{\cdot}32}{12{\cdot}16} = \frac{\text{atomic weight}}{\text{equivalent weight}}$$

or, atomic weight of magnesium = its equivalent weight × its valency

(ii) 9 parts by weight of aluminium replace 1·008 parts by weight of hydrogen from hydrochloric acid, HCl

Hence, the equivalent weight of Al=9
atomic weight of Al=27
and the valency of Al=3 (in $AlCl_3$, valency of Al=3)
$27=9\times3$

i.e., atomic weight of aluminium=its equivalent weight × its valency.

The chemical reactions and equivalent weights. The equivalent weight of an element or a compound depends on the nature of the reaction it undergoes. This will be clear if we analyse the following examples :

$$\begin{array}{llclclcl} \text{(i)} & Fe & + & 2HCl & = & FeCl_2 & + & H_2 \\ & 55{\cdot}85 & & & & & & 2\times1{\cdot}008 \\ \text{(ii)} & 2Fe & + & 3Cl_2 & = & 2FeCl_3 & & \\ & 2\times55{\cdot}85 & & 3\times2\times35{\cdot}46 & & & & \end{array}$$

In the first reaction, the equivalent weight of iron is 55·85/2 =27·925. In the second reaction, the equivalent weight of iron is 2×55·85/3×2 or, 18·616.

If we calculate the equivalent weights of the reactants and products in the above two equations, we find that the number of gram-equivalent of the reactants and products is the same in each of the above reactions. For example,

$$\begin{array}{llclclcl} \text{(i)} & Fe & + & 2HCl & = & FeCl_2 & + & H_2 \\ & 2\times27{\cdot}927 \text{ gram} & & 2\times36{\cdot}46 \text{ gram} & & 2\times63{\cdot}387 \text{ gram} & & 2\times1{\cdot}008 \text{ gram} \\ & 2 \text{ gm.-equiv.} & & 2 \text{ gm.-equiv.} & & 2 \text{ gm.-equiv.} & & 2 \text{ gm.-equiv.} \\ \text{(ii)} & 2Fe & + & 3Cl_2 & = & 2FeCl_3 & & \\ & 6\times18{\cdot}616 \text{ gram} & & 6\times35{\cdot}46 \text{ gram} & & 6\times54{\cdot}076 \text{ gram} & & \\ & 6 \text{ gm.-equiv.} & & 6 \text{ gm.-equiv.} & & 6 \text{ gm.-equiv.} & & \end{array}$$

From the reaction (i) we find that 2 gram-equivalents of iron combine with 2 gram-equivalents of hydrochloric acid to form 2 gram-equivalents of ferrous chloride and 2 gram-equivalents of hydrogen. Hence, in this reaction the number of gram-equivalents of the reactants and products is the same. Again, in the reaction (ii) 6 gram-equivalents of iron react with 6 gram-equivalents of chlorine to form 6 gram-equivalents of ferric chloride. In this case also the number of gram-equivalents of the reactants and products are equal. We arrive at the same conclusion if we analyse the following reactions :

$$\begin{array}{ccccccc} NaOH & + & HCl & = & NaCl & + & H_2O \\ 40 \text{ gram} & & 36{\cdot}47 \text{ gram} & & 58{\cdot}45 \text{ gram} & & 18 \text{ gram} \\ 1 \text{ gram-equiv.} & & 1 \text{ gram-equiv.} & & 1 \text{ gram-equiv.} & & 1 \text{ gram-equiv.} \\ K_2SO_4 & + & BaCl_2 & = & 2KCl & + & BaSO_4 \\ 174{\cdot}2 \text{ gram} & & 208{\cdot}36 \text{ gram} & & 74{\cdot}5 \text{ gram} & & 233{\cdot}36 \text{ gram} \\ 2 \text{ gram-equiv.} & & 2 \text{ gram-equiv.} & & 2 \text{ gram-equiv.} & & 2 \text{ gram-equiv.} \end{array}$$

$Ca(OH)_2$	+	$2HCl$	=	$CaCl_2$	+	$2H_2O$
74·01 gram		72·94 gram		111 gram		36 gram
2 gram-equiv.		2 gram-equiv.		2 gram-equiv.		2 gram-equiv.

Hence, *in all chemical reactions, the numbers of gram-equivalents of the reactants and products are equal.* Therefore, if the equivalent weight of any reactant or product in a chemical reaction is known, the equivalent weights of other substances participating in that reaction can be found out. For example,

CuO	+	H_2	=	Cu	+	H_2O
79·57 gram		$2 \times 1{\cdot}008$ gram		63·57 gram		18 gram
2 gram-equiv.		2 gram-equiv.		2 gram-equiv.		2 gram-equiv.

$$\therefore \ 2 \text{ gram-equivalents} \equiv 79{\cdot}57 \text{ grams of CuO}$$

$$\therefore \ 1 \text{ gram-equivalent} \equiv \frac{79{\cdot}57}{2} = 39{\cdot}78 \text{ grams of CuO}$$

$$\therefore \ \text{The equivalent weight of CuO} = 39{\cdot}78.$$

6.7. Experimental determination of equivalent weights. Generally, equivalent weight of an element can be determined by two methods—(1) Synthesis and (2) Analysis.

(1) **Synthetic method.** In this method, the element whose equivalent weight is to be determined is allowed to combine directly with oxygen or hydrogen or chlorine or their equivalents. For example, hydrogen is burnt in oxygen to form water, or copper in oxygen to form copper oxide in order to determine the ratio H : O or Cu : O.

(2) **Analytical method.** In this method, a compound of the element is analysed and from the data of analysis obtained, the equivalent weight of the element is found out. For example, cupric oxide, CuO, can be reduced by hydrogen to the metallic copper and then the proportion of the metal in the oxide can be determined. From these data, the equivalent weight of copper can be calculated.

Determination of the equivalent weight of non-metals.

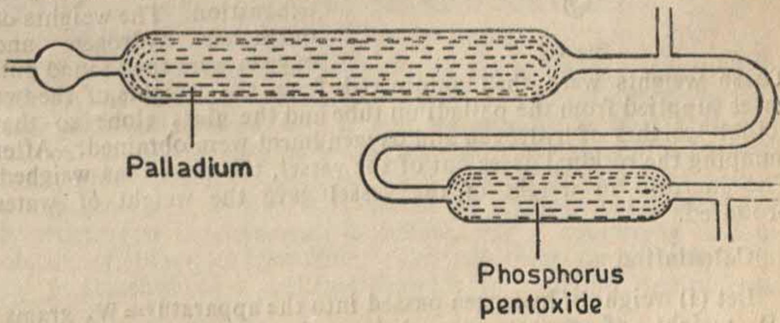

Fig. 6.1

(i) Equivalent weight of hydrogen. Synthesis of hydrides.

The exact determination of the equivalent weight of hydrogen has been made by burning known weight of hydrogen in weighed quantities of oxygen. The procedure described below was first adopted by Morley in 1895.

The pure and dry hydrogen was obtained by absorbing it in palladium in Morley's palladium-tube (Fig. 6·1) and heating the palladium strongly. The tube was weighed before and after the hydrogen had been expelled. Oxygen required for combustion was drawn from large glass globes which was weighed before and after the experiment. The gases were then led in sufficient quantities (so as to produce about 34 grams of water) into the combustion vessel V through the tubes T, T. The vessel V is provided with two jets J, J and a pair of wires S, S for a spark to ignite the gas. The vessel had been previously evacuated and weighed. Hydrogen and oxygen were then burnt at the platinum jets to produce steam. During burning, the vessel was immersed in cold water. The water collecting in the vessel was then frozen by dipping the lower part into a freezing mixture. The unreacted gases were pumped out of the vessel through the tube T, T and analysed. The tubes T, T were packed with phosphorus pentoxide in order to prevent the escape of water vapour on exhaustion. The weights of unreacted hydrogen and oxygen were then found out. These weights were then subtracted from the weights of the two gases supplied from the palladium tube and the glass globe so that actual weights of hydrogen and oxygen burnt were obtained. After pumping the residual gases out of the vessel, the vessel was weighed. The increase in weight of the vessel gave the weight of water produced.

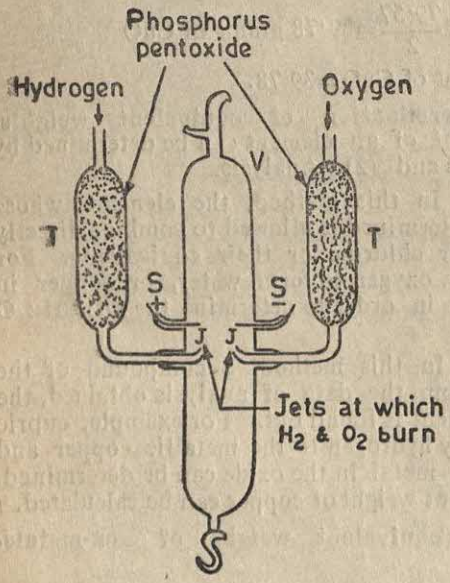

Fig. 6.2

Calculation

Let (i) weight of hydrogen passed into the apparatus $= W_1$ grams. (ii) weight of oxygen passed into the apparatus $= W_2$ grams. (iii) weight of unreacted hydrogen $= W_3$ grams. (iv) weight of unreacted oxygen $= W_4$ grams. (v) weight of water produced $= W_5$

grams. weight of hydrogen burnt$=(W_1-W_3)$ grams weight of oxygen burnt$=(W_2-W_4)$ grams.

Therefore, (W_2-W_4) grams of oxygen reacted with (W_1-W_3) grams of hydrogen.

$\therefore$ 8 grams of oxygen reacted with $\dfrac{(W_1-W_3)}{(W_2-W_4)}\times 8$ grams of hydrogen.

Hence, the equivalent weight of hydrogen$=\dfrac{W_1-W_3}{W_2-W_4}\times 8$

The value of the equivalent weight of hydrogen found by Morley was 1·0076.

(ii) **Equivalent weight of chlorine. Synthesis of hydrides.** The equivalent weight of chlorine can be determined accurately by burning known weights of hydrogen in weighed quantities of chlorine and weighing hydrogen chloride produced :

$$H_2+Cl_2=2HCl$$

This method was first described by Edgar in 1908. Chlorine was prepared by the electrolysis of fused silver chloride. It was then condensed to liquid and weighed in the liquid state. The pure and dry hydrogen was obtained by absorbing it in palladium in palladium-tube and heating the palladium strongly. The tube was weighed before and after the hydrogen had been expelled. The hydrogen and chlorine were led into a quartz bulb which was previously evacuated and weighed. The gases were ignited into the bulb by an electric spark. The hydrogen chloride thus produced was then condensed to a liquid in a nickel-plated steel bomb by means of liquid air and weighed. If W_1 grams of chlorine are found to combine with W_2 grams of hydrogen, then the equivalent weight of chlorine is given by $\dfrac{W_1}{W_2}\times 1{\cdot}008$.

(iii) **Equivalent weight of carbon. By synthesis and analysis of the oxide of carbon.** The equivalent weight of carbon can be determined by burning a weighed quantity of carbon in pure and dry oxygen. The carbon dioxide formed is then weighed.

$$C+O_2=CO_2\;;\;CO+CuO=CO_2+Cu$$

The apparatus depicted in the figure 6·3 is set up. A porcelain boat (A) is cleaned and dried. About 1 gram of freshly ignited sugar charcoal is placed into it and weighed. The boat with the charcoal is placed into a hard-glass tube together with a layer of freshly ignited copper oxide (B). One end of the hard-glass tube is attached to a U-tube (C) containing calcium caloride whilst the other end is connected to potash bulbs containing strong solution of potassium hydroxide. The exit from the potash bulbs (D) is attached to a calcium-chloride tube (E) to prevent loss of moisture from the solution of potassium hydroxide. Before experiment the potash bulbs are weighed full of oxygen because after the experiment it will be filled with this gas. A slow stream of dry and pure oxygen is then passed through the glass tube and the boat and the layer of cupric oxide are strongly heated with Bunsen burners. The charcoal burns in oxygen to carbon dioxide but a small quantity of carbon monoxide is simultaneously produced. Carbon monoxide is oxidised by red-hot cupric oxide to carbon dioxide. The carbon dioxide passes into the potash bulbs where it is absorbed by alkali. After the charcoal has been completely burnt the burners are turned out but oxygen is passed through the tube for some time in order to sweep all the carbon dioxide out of the hard-glass tube into the potash bulbs. The boat and potash bulbs are reweighed in order to find the weight of carbon that has been burnt and the weight of the resulting carbon dioxide.

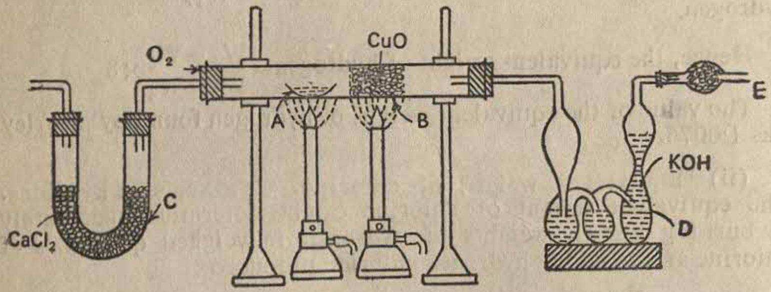

Fig. 6.3

Calculation. Let us suppose that

(i) Weight of boat containing charcoal before experiment= W_1 grams.

(ii) Weight of boat after experiment $= W_2$ grams.

$\therefore$ Weight of charcoal burnt $= (W_1 - W_2)$ grams.

(iii) Weight of potash bulbs before experiment $= W_3$ grams.

(iv) Weight of potash bulbs after experiment $= W_4$ grams.

$\therefore$ Weight of carbon dioxide formed $= (W_4 - W_3)$ grams.

Hence, the weight of oxygen combining with charcoal $= [(W_4 - W_3) - (W_1 - W_2)]$ grams.

Therefore, $[(W_4 - W_3) - (W_1 - W_2)]$ parts by weight of oxygen combine with $(W_1 - W_2)$ parts by weight of charcoal.

$\therefore$ 8 parts by weight of oxygen combine with

$\dfrac{(W_1 - W_2) \times 8}{(W_4 - W_3) - (W_1 - W_2)}$ parts by weight of carbon.

Hence, the equivalent weight of carbon is $\dfrac{(W_1 - W_2) \times 8}{(W_4 - W_3) - (W_1 - W_2)}$

(iv) Determination of equivalent weight of oxygen. When pure and dry hydrogen is passed over cupric oxide, it reduces cupric oxide to copper and forming water :

$$CuO \quad + \quad H_2 \quad = \quad Cu \ + \ H_2O$$

Knowing the decrease in weight of cupric oxide and weight of water produced it is possible to determine the equivalent weight of oxygen.

Procedure. A small quantity of pure and dry cupric oxide is taken in a hard-glass tube (B) and its weight is determined. The purified and dried hydrogen is passed through a bulb-tube containing anhydrous calcium chloride and then into the tube (B). The tube (B) is connected to a weighed U-tube (C) containing fused calcium chloride. The tube (B) is heated ; hydrogen combines with cupric oxide forming water which passes off in the form of vapour and is absorbed by calcium chloride in the U-tube (C). The whole apparatus is now cooled in a current of hydrogen and the tube (B) and the U-tube (C) are weighed accurately.

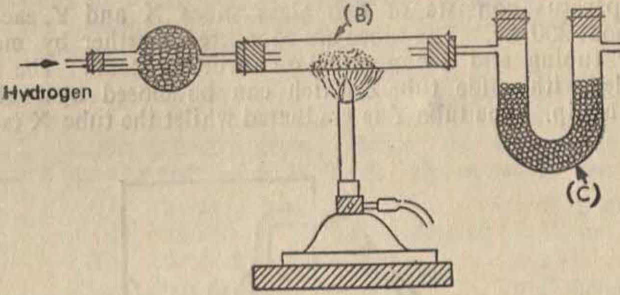

Fig. 6.4

Calculation. Let us suppose that
the weight of the tube (B) + CuO before reaction $= a$ grams
the weight of the tube (B) + CuO + Cu after reaction $= b$ grams
the weight of calcium chloride tube (C) before the experiment $= c$ grams
the weight of calcium chloride tube (C) after the experiment $= d$ grams.

Hence, the weight of oxygen which has combined with hydrogen $= (a - b)$ grams.

The weight of water formed $= (d - c)$ grams

Therefore, $(a - b)$ grams of oxygen are present in $(d - c)$ grams of water ; hence the weight of hydrogen reacted is $\{(d - c) - (a - b)\}$ grams.

Now $\{(d-c)-(a-b)\}$ grams of hydrogen react with $(a-b)$ grams of oxygen.

Hence, the equivalent weight of oxygen

$$=\frac{(a-b)\times 1{\cdot}008}{\{(d-c)-(a-b)\}}$$

Determination of equivalent weights of metals. (i) Equivalent weight of zinc by displacement of hydrogen. The equivalent weight of zinc is determined by allowing a weighed quantity of zinc to react with excess of moderately concentrated hydrochloric acid and measuring the volume of hydrogen liberated. The apparatus employed in the determination is the Ostwald's gas buret (Fig. 6·5).

The apparatus consists of two glass tubes X and Y, each of capacity about 200 c.c. The tubes are connected together by means of a rubber tubing and are mounted on a wooden stand. The tube X is provided with a side tube Z which can be closed by a rubber tubing and a clip. The tube Y is graduated whilst the tube X is not graduated and is open. The conical flask M is connected to the tube Y. The tubes X and Y are filled with water upto the zero graduation mark in Y at the start of the experiment and the water levels in X and Y must be made equal. A piece of zinc is placed in the conical flask M. A small test tube filled with moderately strong hydrochloric acid is lowered gently and carefully into the conical flask. The conical flask is then connected to the tube Y by means of a glass

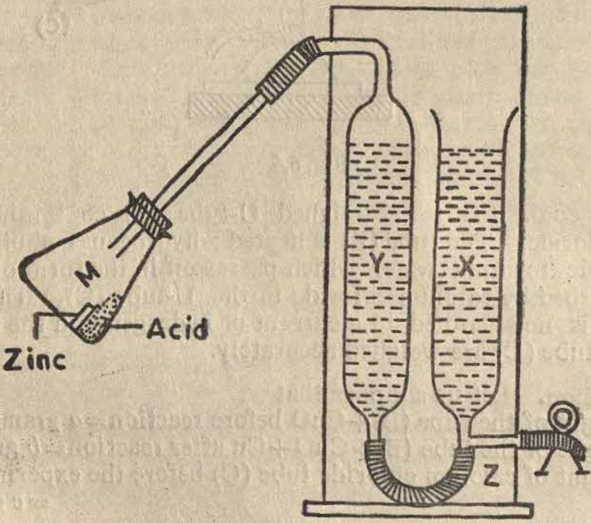

Fig. 6.5

tube and a rubber tubing as shown in the figure. If the water levels in X and Y are not equal at this time, some water is run out of the side tube Z until the levels become equal. The level of water in Y is noted. The conical flask is then shaken gently and the test tube falls over when the acid comes in contact with the zinc granule and the reaction starts. Hydrogen evolved passes into the tube Y, when water level in Y is lowered and the level in X is raised. When the reaction is complete, the water in Y and X is adjusted to the same level by running water out of the side tube Z. The level of water in Y is noted. The difference between the initial and final readings of the water level in Y gives the volume of hydrogen liberated at the temperature of the room. The barometric pressure and room temperature are recorded.

Calculation. The calculation is based upon the fact that 22·4 litres of hydrogen at N.T.P. weigh 2 grams. Or, 1 c.c. of hydrogen at N. T. P. weighs 0·00009 gram. Hence, the volume of hydrogen measured must be reduced to N. T. P. Let us assume that

(i) the weight of zinc $=$ W grams.
(ii) volume of hydrogen collected $= V_1$ c.c.
(iii) temperature of water $= t$ C.
(iv) barometric pressure $=$ P mm. of Hg.
(v) aqueous tension at t°C $= f$ mm.

Now, barometric pressure = pressure of hydrogen + aqueous tension at t°C.

$\therefore$ $P = \text{pressure of hydrogen} + f$

Or, pressure of hydrogen $= (P - f)$ mm. of Hg.

Let V_2 c.c. be the volume of hydrogen at N.T.P. Then,

$$\frac{760 \times V_2}{273} = \frac{(P-f) \times V_1}{(273+t)} \quad \text{or,} \quad V_2 = \frac{(P-f) \times V_1 \times 273}{760 \times (273+t)} \text{ c.c.}$$

The weight of V_2 c.c. of hydrogen at N.T.P. $= V_2 \times 0{\cdot}00009$

$$= \frac{(P-f) \times V_1 \times 273}{760 \times (273+t)} \times 0{\cdot}00009 \text{ grams.}$$

$$\therefore \text{ Equivalent weight of zinc} = \frac{W \times 1{\cdot}008}{V_2 \times 0{\cdot}00009}$$

$$= \frac{W \times 1{\cdot}008 \times 760 \times (273+t)}{(P-f) \times V_1 \times 273 \times 0{\cdot}00009}$$

N. B. (i) Since pure zinc does not react with acid a few drops of copper sulphate solution are added to the solution. A small amount of zinc is lost due to the following reaction :

$$Zn + CuSO_4 = ZnSO_4 + Cu$$

Since very small quantity of copper sulphate is added the loss of zinc due to the above reaction is so small that it does not introduce any appreciable error in the equivalent weight of zinc.

(ii) A small amount of zinc must be taken so that the hydrogen evolved is conveniently collected in the graduated tube. The weight of zinc taken in this case should not exceed 0·1 gram.

(iii) Excess of acid must be taken so that zinc completely dissolves in acid.

This method can also be used to determine the equivalent weight of magnesium by dissolving it in dilute sulphuric acid or of aluminium by dissolving it in caustic soda.

$Mg+H_2SO_4=MgSO_4+H_2$; $2Al+2NaOH+2H_2O=2NaAlO_2+3H_2$

Determination of equivalent weights by oxide formation method. A weighed quantity of a metal is completely converted into its oxide and the weight of the oxide formed is determined. The weight of combined oxygen is then determined by subtracting the weight of the metal from the weight of its oxide. The parts by weight of the metal combining with 8 parts by weight of oxygen gives the equivalent weight of metal.

$$\text{Equivalent weight of the metal}=\frac{\text{Weight of the metal}\times 8}{\text{Weight of combined oxygen}}.$$

Equivalent weight of magnesium by the synthesis of magnesium oxide. A porcelain crucible and its lid are cleaned, dried and weighed. The processes of drying and weighing are repeated till a constant weight is obtained. Then a piece of cleaned magnesium ribbon is placed in the crucible which is then weighed again with the lid ; the crucible is then placed on a clay-pipe triangle with its lid put slightly on one side in order to admit air into the crucible. The crucible is now heated in the Bunsen flame, when magnesium is converted to oxide. When the conversion is complete, the crucible is cooled in a desiccator and weighed. The process of heating and weighing is repeated till a constant weight is obtained.

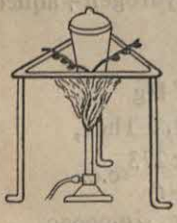
Fig. 6.6

Calculation. Let us suppose that

Weight of empty crucible + lid = W_1 grams.
Weight of crucible + lid + magnesium = W_2 grams.
Weight of crucible + lid + magnesium oxide = W_3 grams.
$\therefore$ Weight of magnesium = (W_2-W_1) grams.

and weight of oxygen combined with the element = (W_3-W_2) grams.

Hence, (W_3-W_2) grams of oxygen combine with $(W\ -W_1)$ grams of magnesium.

$\therefore$ 8 grams of oxygen combine with $\frac{(W_2-W_1)\times 8}{(W_3-W_2)}$ gram of magnesium.

Therefore, the equivalent weight of Mg$=\dfrac{(W_2-W_1)\times 8}{(W_3-W_2)}$.

This method of determining the equivalent weight of magnesium is unsatisfactory due to the following reasons :

(i) The conversion to oxide is liable to be incomplete.
(ii) A portion of magnesium oxide may escape to the atmosphere.
(iii) A small amount of magnesium nitride Mg_3N_2 may be formed.

Equivalent weight of copper by synthesis of oxide. A porcelain crucible and its lid are taken and its weight is determined. Then a piece of pure copper wire is taken into the crucible and the weight of the crucible together with the copper wire is determined. Conc. nitric acid is added drop by drop till the metal dissolves completely. The solution thus obtained is evaporated to dryness on a water-bath when a green residue of copper nitrate is left into the crucible. Care should be taken to see that none of copper nitrate is lost by spirting during evaporation. The crucible with the green residue is now placed on a clay-pipe triangle and strongly heated, when copper nitrate is converted into black copper oxide. When the conversion is complete, the crucible and the lid are allowed to cool in a desiccator and weighed. The process of heating and cooling is repeated till the final weight is constant.

$$3Cu+8HNO_3=3Cu(NO_3)_2+4H_2O+2NO$$
$$2Cu(NO_3)_2=2CuO+4NO_2+O_2$$

Calculation. Let us suppose that

Weight of the crucible+lid$=W_1$ grams.

Weight of the crucible+lid+copper wire$=W_2$ grams.

Weight of the crucible+lid+copper oxide$=W_3$ grams.

$\therefore$ Weight of copper reacted$=(W_2-W_1)$ grams.

and the weight of oxygen combined with copper$=(W_3-W_2)$ grams.

Therefore, (W_3-W_2) grams of oxygen combine with (W_2-W_1) grams of copper.

8 grams of oxygen combine with $\dfrac{(W_2-W_1)\times 8}{(W_3-W_2)}$ gram of Cu

Hence, the equivalent weight of copper is $\dfrac{(W_2-W_1)\times 8}{(W_3-W_2)}$.

The equivalent weight of tin or zinc can be determined by this process.

Equivalent weight of iron, copper, etc., by the analysis of their oxides. The equivalent weights of copper, iron, etc., can be determined by heating a weighed quantity of the oxides of the metals in a stream of hydrogen or purified coal gas when the oxide is reduced to the metal. The metal formed is weighed.

Calculation. Let us suppose that

(i) Weight of metal oxide taken $= W_1$ grams.

(ii) Weight of metal formed $= W_2$ grams.

∴ Weight of oxygen combining with the metal $= (W_1 - W_2)$ gram.

Hence, $(W_1 - W_2)$ grams of oxygen combine with W_2 grams of metal.

8 grams of oxygen combine with $\frac{W_2 \times 8}{(W_1 - W_2)}$ grams of the metal.

Therefore, the equivalent weight of metal $= \frac{W_2 \times 8}{(W_1 - W_2)}$.

The equivalent weight of silver by synthesis of chloride. A weighed quantity of pure silver is dissolved into nitric acid. The solution of silver nitrate thus obtained should be slightly acidic. The solution is heated and very pure hydrochloric acid is then added drop by drop into the solution till the precipitation is complete. It is then filtered through a tared filter-paper ; the precipitates on the filter paper are washed first with water containing little nitric acid and finally with distilled water till the removal of acid is complete. The precipitates are dried in air-oven at 130°C. It is then cooled in a desiccator and weighed. The process of drying, cooling and weighing is repeated till a constant weight is obtained.

Calculation. Let us assume that

weight of silver taken $= W_1$ grams.

weight of silver chloride formed $= W_2$ grams.

∴ weight of chlorine combining with silver $= (W_2 - W_1)$ grams.

Hence, $(W_2 - W_1)$ grams of chlorine combine with W_1 grams of silver.

∴ 35·46 grams of chlorine combine with $\frac{W_1 \times 35{\cdot}46}{(W_2 - W_1)}$ grams of silver.

Therefore, the equivalent weight of silver is $\frac{W_1 \times 35{\cdot}46}{(W_2 - W_1)}$.

Equivalent weight of sodium and potassium by analysis of halides. A known weight of potassium chloride or sodium chloride is dissolved into distilled water containing little nitric acid. Excess of silver nitrate solution is added to the solution when curdy white precipitates of silver chloride are formed. The precipitates are filtered, washed with distilled water and dried in air-oven. It is cooled in a desiccator and weighed.

$$NaCl + AgNO_3 = AgCl + NaNO_3$$

Calculation. Let

(i) weight of sodium chloride $= W_1$ grams.
(ii) weight of silver chloride precipitated $= W_2$ grams.

Now, it is known that $143{\cdot}34 = (107{\cdot}88 + 35{\cdot}46)$ grams of silver chloride contain 35·46 grams of chlorine.

W_2 grams of silver chloride contain $\frac{35{\cdot}46 \times W_2}{143{\cdot}34}$ gram of chlorine.

Hence, $\frac{35{\cdot}46 \times W_2}{143{\cdot}34}$ grams of chlorine has been derived from W_1 grams of sodium chloride.

Therefore, the weight of sodium combining with $\frac{35{\cdot}46 \times W_2}{143{\cdot}34}$ grams of chlorine is $\left(W_1 - \frac{35{\cdot}46 \times W_2}{143{\cdot}34}\right)$ grams.

Hence, the equivalent weight of sodium is

$$\frac{\left(W_1 - \frac{35{\cdot}46 \times W_2}{143{\cdot}34}\right) \times 35{\cdot}46}{\frac{35{\cdot}46 \times W_2}{143{\cdot}34}} = \frac{(143{\cdot}34W_1 - 35{\cdot}46W_2)}{W_2}$$

The equivalent weight of the light metals whose chlorides are soluble in water can be determined by this method.

Equivalent weight of metals by interchange of radicals. The equivalent weight of a metal can be deduced by comparing the weights of two of its salts. Thus, if a known weight of a salt MR_1 is converted into another salt MR_2 whose weight can be experimentally determined, then the equivalent weight of the metal M can be found out, provided the equivalents of the radicals R_1 and R_2 are known. The method is explained by describing the procedure adopted for determining the equivalent weight of barium.

A known amount of barium chloride is dissolved into distilled water containing little HCl. Then excess of sulphuric acid is added to it when all the barium is precipitated as barium sulphate. The reaction that takes place is

$$BaCl_2 + H_2SO_4 = BaSO_4 + 2HCl$$

The precipitate is filtered, washed with water, dried and finally weighed.

Calculation. Let us assume that

weight of barium chloride taken $= W_1$ grams.
weight of barium sulphate precipitated $= W_2$ grams.
the equivalent weight of chlorine $= 35{\cdot}46$
the equivalent weight of sulphate $= 48$

Let the equivalent weight of barium be x

Then, the equivalent weight of barium chloride $= x + 35{\cdot}46$

the equivalent weight of barium sulphate $= x + 48$.

Therefore, $(x+35{\cdot}46)$ parts by weight of barium chloride give $(x+48)$ parts by weight of barium sulphate.

Or, 1 part by weight of barium chloride give $\frac{(x+48)}{(x+35{\cdot}46)}$ parts by weight of barium sulphate.

Again, from the experimental result we get

W_1 parts by weight of barium chloride yield W_2 parts by weight of barium sulphate.

Or, 1 part by weight of barium chloride yield $\frac{W_2}{W_1}$ parts by weight of barium sulphate.

Hence, $\frac{x+48}{x+35{\cdot}46} = \frac{W_2}{W_1}$, whence x can be found out.

Determination of the equivalent weight of a metal by displacement of one metal by another. This method is based upon the fact that a more "electropositive" metal displaces a less electropositive metal from its salt in solution. Thus, zinc displaces copper from copper sulphate; iron also displaces copper from copper sulphate solution.

$$Zn + CuSO_4 = ZnSO_4 + Cu$$
$$Fe + CuSO_4 = FeSO_4 + Cu$$

Therefore, the equivalent weight of one metal can be determined provided the equivalent weight of the other is known. The method, however, is not usually suitable for exact measurement because the precipitate of finely divided metal which is displaced is often too impure for the purpose.

Equivalent weight of iron. A solution of very pure copper sulphate is taken into a beaker and weighed quantity of clean and pure iron powder is added to the solution. Iron dissolves into the solution and red copper begins to precipitate at the bottom of the beaker. When all the iron powder has been dissolved, the precipitates of red copper are filtered through a previously weighed filter paper. The precipitates are washed with distilled water until the wash-water is no longer coloured blue. Then it is washed with alcohol and dried in air-oven and weighed.

Calculation. Let
(i) weight of iron powder dissolved $= W_1$ grams.
(ii) weight of filter paper $= W_2$ grams.
(iii) weight of filter paper + precipitate of copper $= W_3$ grams.

The equivalent weight of copper is known to be 31·5

$\therefore$ weight of copper displaced $= (W_3 - W_2)$ grams.

Hence, $(W_3 - W_2)$ grams of copper are displaced by W_1 grams of iron. Or, 31·5 grams of copper are displaced by $\frac{W_1 \times 31{\cdot}5}{W_3 - W_2}$ grams of iron.

Hence, the equivalent weight of iron $= \frac{W_1 \times 31{\cdot}5}{(W_3 - W_2)} = x$ (say)

From this expression we can arrive at a very important conclusion :

$$x = \frac{W_1 \times 31{\cdot}5}{W_3 - W_2} \quad \text{or,} \quad \frac{x}{31{\cdot}5} = \frac{W_1}{W_3 - W_2}$$

$$\text{or,} \quad \frac{\text{equivalent weight of iron}}{\text{equivalent weight of copper}} = \frac{\text{weight of iron dissolved}}{\text{weight of copper deposited}}$$

Thus, in general we can write

$$\frac{\text{equivalent weight of one metal, } M_1}{\text{equivalent weight of another metal, } M_2} = \frac{\text{weight of metal } M_1 \text{ dissolved}}{\text{weight of metal } M_2 \text{ deposited}}.$$

Thus, the weight of a metal deposited from the solution of its salt is proportional to the equivalent weight of the metal.

Equivalent weight of metals by the application of the laws of electrolysis. This method is based on Faraday's second law of electrolysis. The law states that if the same quantity of electricity is passed for the same time through a number of solutions of different electrolytes, the weights of different substances deposited at the electrodes are proportional to their chemical equivalents.

The principle can be illustrated by describing the method for the determination of the equivalent weight of copper.

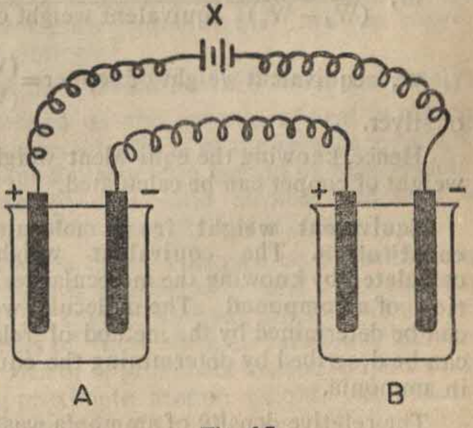

Fig. 6.7

The cell A contains copper sulphate solution in which copper electrodes are dipped and the cell B contains silver nitrate solution in which silver electrodes are dipped. Before experiment the electrodes are carefully cleaned, dried and weighed. The two cells A and B are connected in series with an accumulator X and electric current is passed. After some time when sufficient quantity of copper and silver have been deposited on the cathode, the current is switched off. The cathodes from the cells A and B are withdrawn. They are washed first with distilled water and then alcohol, dried and weighed.

Calculation. Let

(i) the weight of cathode in the cell A before electrolysis $=W_1$ grams.

(ii) the weight of cathode in the cell A after electrolysis $=W_2$ grams.

$\therefore$ weight of copper deposited$=(W_2-W_1)$ grams.

(iii) the weight of cathode in the cell B before electrolysis $=W_3$ grams.

(iv) the weight of cathode in the cell B after electrolysis $=W_4$ grams.

$\therefore$ weight of silver deposited$=(W_4-W_3)$ grams.

From Faraday's law

$$\frac{\text{weight of copper deposited}}{\text{weight of silver deposited}}=\frac{\text{equivalent weight of copper}}{\text{equivalent weight of silver}}$$

$$\text{or, } \frac{(W_2-W_1)}{(W_4-W_3)}=\frac{\text{equivalent weight of copper}}{\text{equivalent weight of silver}}$$

or, equivalent weight of copper$=\dfrac{(W_2-W_1)}{(W_4-W_3)}\times$equivalent weight of silver.

Hence, knowing the equivalent weight of silver, the equivalent weight of copper can be calculated.

Equivalent weight from molecular weight and molecular constitution. The equivalent weight of an element can be calculated by knowing the molecular weight and molecular constitution of a compound The molecular weight of a gaseous compound can be determined by the method of relative density. The method can be described by determining the equivalent weight of nitrogen in ammonia.

The relative density of ammonia was determined to be 8·516 and hence its molecular weight is 17·032. The molecular constitution of ammonia is known to be NH_3. Hence, the weight of nitrogen which combine with $3 \times 1{\cdot}008$ grams of hydrogen is $17{\cdot}032 - 3{\cdot}024 = 14{\cdot}008$ grams of nitrogen. Hence, 1·008 grams of hydrogen combine with 4·669 grams of nitrogen. Therefore, the equivalent weight of nitrogen is 4·669.

6.8. Determination of atomic weight from equivalent weight. It has been shown that atomic weight and equivalent weight of an element are simply related as :

Atomic weight = equivalent weight × valency.

This relation permits the determination of exact atomic weight of the element. The procedure adopted consists of the following steps :

(i) Determination of equivalent weight. Equivalent weights can be accurately found out by chemical analysis. The various methods have been discussed above.

(ii) Deduction of valency of the element. Approximate atomic weight of the element is determined. The valency is next deduced by dividing the approximate atomic weight by the equivalent weight and taking the nearest integer as the correct number, since valency is always a whole number. Approximate atomic weight is determined by one of the methods set out below :

(a) **From molecular weight and atomicity of gaseous element (Avogadro's method).** This method has been described in Chapter IV.

(b) **Cannizzaro's method.** This method of determining the atomic weight of elements has been described in Chapter IV.

(c) **Dulong and Petit's method.** This method of determining the approximate atomic weight is applicable to the solid elements. It is based on the law of Dulong and Petit which states that the product of the atomic weight of a solid element and its specific heat at room temperature is approximately equal to 6.4. We can express the law in algebraic form as follows :

Specific heat × atomic weight = atomic heat = 6·4 (approximately)

The specific heat is defined as the amount of heat in calories required to raise the temperature of 1 gram of the substance by 1°C. Therefore, it can be measured easily with the aid of a calorimeter. The approximate atomic weight of a solid element can then be easily calculated by dividing 6·4 by its specific heat.

Limitations of Dulong-Petit's law. This method of determining the approximate atomic weight is applicable to solid elements only. Moreover, the law fails in the case of carbon, silicon, boron and beryllium. The atomic heats of these elements are much less than 6·4. The law only gives an idea of approximate atomic weights of the elements. But from this approximate atomic weight, exact atomic weight can be obtained with the help of the following relationship :

Atomic weight = valency × equivalent weight.

Isomorphism. Different substances of similar chemical character are able to crystallise in the same crystalline form. Thus, potash alum, chrome alum, etc., have the same crystalline form. Phosphates and arsenates of similar composition and containing the same number of water of crystallisation crystallise in the same crystalline form. Such substances which have the same crystalline structure and similar chemical composition are said to be isomorphous with one another. The phenomenon of occurrence of different substances of similar chemical composition in the same crystalline form is known as *isomorphism*. Isomorphous crystals have the same geometric form, same number of faces and have equal angles of intersection between corresponding faces.

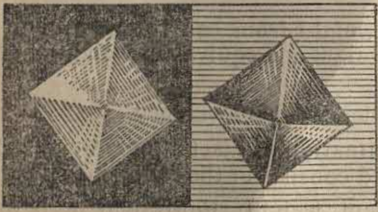
Fig. 6.8 : Isomorphous crystals of aluminium and chrome alum.

But the reverse is not always true, i.e., the substances having the similar crystalline structure may not be isomorphous. For example, the crystal of sodium chloride and that of diamond have the same crystalline form but they are not isomorphous with one another.

Criteria of Isomorphism. The following are the criteria of isomorphism :

(i) Isomorphous substances have similar crystalline structure.

(ii) They are frequently able to form mixed crystals. For example, when a solution containing chrome alum and potash alum is crystallised, the crystals will contain both alums. These crystals are called mixed crystals. Mixed crystals are, therefore, homogeneous mixture of two or more isomorphous substances in a single crystalline form. Hence, the name **solid solution** for them is more appropriate.

(iii) Crystals of isomorphous substances are able to form overgrowths. When a crystal of a substance is suspended in a slightly supersaturated solution of an isomorphous substance, the crystal will grow in size. For example, when a purple crystal of chrome alum is suspended in a slightly supersaturated solution of potash alum, the potash alum will be deposited in chrome alum. Consequently, the crystal will grow in size, preserving its original geometrical form. In this process, potash alum has formed an overgrowth on the chrome alum.

(iv) Isomorphous substances have analogous chemical constitution. If we examine carefully a series of isomorphous compounds, a parallelism of chemical structure in them becomes obvious. For example, K_2SO_4 and Rb_2SO_4 have the same type of molecular structure.

Isomorphism is due to the fact that atoms or ions of approximately equal size and with equal charges can substitute one another in the crystal lattice without affecting its stability. Thus the radii of chloride and bromide ion are quite close to one another (1·81Å and 1·96Å respectively), and have the same charge. Hence, the crystals of KCl and KBr are isomorphous with one another and they form mixed crystals. On the other hand, the radii of sodium ion and potassium ion are quite different (0·93Å and 1·33Å respectively) and hence sodium ion and potassium ions cannot substitute one another in crystals. Hence, sodium chloride and potassium chloride are not isomorphous and do not form mixed crystals, although they are chemically similar.

A few examples of isomorphous substances are given below :

(i) Zinc sulphate, $ZnSO_4, 7H_2O$ and ferrous sulphate $FeSO_4, 7H_2O$.

(ii) Potassium sulphate, K_2SO_4 and potassium chromate K_2CrO_4.

(iii) Potash alum, $K_2SO_4, Al_2(SO_4)_3, 24H_2O$ and chrome alum, $K_2SO_4, Cr_2(SO_4)_3, 24H_2O$.

(iv) Sodium dihydrogen phosphate, NaH_2PO_4, H_2O and sodium dihydrogen arsenate NaH_2AsO_4, H_2O.

From the formulas of the above substances, it is evident that each of the molecules of two isomorphous substances contains equal* number of atoms and have the similar composition. The number of atoms of the two different elements in the two isomorphous substances is the same and if one atom is replaced by the other there is no change in the crystalline structure. For example, if chromium atom in potassium clromate crystal is replaced by sulphur atom, the crystalline form of potassium chromate crystals remains unaltered, and we will get potassium sulphate crystals.

Mitscherlich studied a large number of isomorphous crystals and enunciated a law known as Mitscherlich's law of isomorphism. The law may be stated as :

Equal number of atoms united in the same way form isomorphous crystals. The crystalline form of these crystals depends only on the number of atoms in their molecules and the way in which they are combined but is independent of their chemical properties.

The law may be stated in another way :

Substances which are isomorphous with each other (i.e., having similar crystalline form and chemical properties) can usually be represented by similar formulas.

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* In few cases it is found that although the two crystals are isomorphous and have similar chemical composition, they contain different number of atoms, e g., K_2SO_4 & $(NH_4)_2SO_4$.

Thus, zinc sulphate and ferrous sulphate are similar in crystalline form and in chemical properties. They can be represented by formulas :

$$ZnSO_4, 7H_2O \text{ and } FeSO_4, 7H_2O$$

One formula can be changed into the other merely by writing Fe for Zn. Isomorphous phosphates and arsenates can be represented by the similar formulas,

$$NaH_2PO_4, H_2O \text{ and } NaH_2AsO_4, H_2O$$

This pair of isomorphous compounds contains the same number of atoms and P can replace As without changing its crystalline form and this replacement takes place atom for atom. This means that 31 parts of phosphorus are replaced by 75 parts of arsenic on passing from one compound to the other, 31 and 75 being the atomic weights of phosphorus and arsenic respectively. Thus, if two elements are interchangeable in a pair of isomorphous compounds and if the atomic weight of one of the two elements is known, we can calculate the atomic weight of the other. The method of calculation is illustrated below :

Let us suppose that AR and BR are two isomorphous compounds, the atomic weight of A (say m) is known, that of B (say n) is to be determined. The percentage of R in both the compounds can be determined by chemical analysis. Let the percentage of R in AR and BR be x and y respectively, then

In AR ; $(100-x)$ grams of A combine with x grams of R.

In BR ; $(100-y)$ grams of B combine with y grams of R.

or, $\frac{(100-y)\times x}{y}$ grams of B combine with x grams of R.

Hence, $\frac{(100-y)x}{y}$ grams of B can replace $(100-x)$ grams of A from AR. Or, $\frac{(100-y)x}{y\times n}$ atoms of B can replace $\frac{(100-x)}{m}$ atoms of A from AR, where n and m are the atomic weights of B and A respectively. By the law of isomorphism, the number of atoms of B replacing the number of atoms of A must be equal.

Hence, we get, $$\frac{100-x}{m}=\frac{(100-y)\times x}{y\times n}$$

or, $$\frac{n}{m}=\frac{(100-y)\times x}{(100-x)\times y}$$

Since, x, y and m are known, n the atomic weight of B can be calculated.

(b) Let us suppose that there are two different elements A and B in two isomorphous substances, and their atomic weights are respectively a and b. Let us suppose further that x grams of A in one compound replace y grams of B from the other compound.

Now, the number of gram-atoms in x grams of $A=\frac{x}{a}$

The number of gram-atoms in y grams of $B=\frac{y}{b}$

According to Mitscherlich's law of isomorphism,

$$\frac{x}{a}=\frac{y}{b} \qquad \therefore \frac{x}{y}=\frac{a}{b}$$

$$\text{or, } \frac{\text{replaced weight of A}}{\text{replaced weight of B}}=\frac{\text{atomic weight of A}}{\text{atomic weight of B}}$$

Hence, if the replaced weights of A and B are known and atomic weight of one element is known, then the atomic weight of the other element can be determined.

Determination of valency of an element by Mitscherlich's law of isomorphism.

The valency of an element can be known exactly with the help of Mitscherlich's law of isomorphism. The different elements in two or more isomorphous substances have the same valency. Hence if the valency of one element is known, that of the other element can be determined. For example, aluminium oxide, chromic oxide and ferric oxide are isomorphous. The formula of aluminium oxide is Al_2O_3 and the valency of aluminium is 3. Hence the formula of chromic oxide is Cr_2O_3 and the valency of chromium is 3. Similarly, the formula of ferric oxide is Fe_2O_3 and the valency of iron in this compound is 3.

Determination of atomic weights by chemical analysis (Stas and Richard's method). In this method, the reactants and products are weighed accurately and the ratio of their weights is determined. Then the atomic weight of the element is determined by taking the atomic weight of oxygen to be 16. The method is explained with an example.

(i) A known weight of $KClO_3$ is completely decomposed into KCl and oxygen. Then the weight of KCl is accurately found out. The ratio of the weight of KCl and oxygen is next found out. Let us suppose that

$$\frac{\text{weight of KCl}}{\text{weight of oxygen}}=x$$

(ii) A known weight of KCl is dissolved in water and then excess of $AgNO_3$-solution is added to it, when AgCl is precipitated. The precipitate of AgCl is washed, dried and accurately weighed. Let us suppose that $\frac{\text{weight of AgCl}}{\text{weight of KCl}}=y$

(iii) A known weight of silver is completely dissolved in nitric acid when a solution of silver nitrate is obtained. Excess of KCl-solution is then added to the solution when silver is completely precipitated in the form of silver chloride. The precipitate of AgCl is filtered, washed, dried and weighed. Then its weight is determined. Let us suppose that

$$\frac{\text{weight of silver chloride}}{\text{weight of silver}}=z.$$

Calculation. The following data are obtained from the above experiment.

$$\text{(i)}\ \frac{\text{weight of KCl}}{\text{weight of } O_2}=x \quad \text{(ii)}\ \frac{\text{weight of AgCl}}{\text{weight of KCl}}=y$$

$$\text{(iii)}\ \frac{\text{weight of AgCl}}{\text{weight of Ag}}=z$$

Let the atomic weights of K, Cl and Ag are respectively a, b and c. Taking the atomic weight of oxygen to be 16, we get

(i) $\frac{a+b}{3\times16}=x$ [$\because$ 1 gram-mole of $KClO_3$ contain 1 gram-mole of KCl and 48 grams of oxygen]

(ii) $\frac{c+b}{b+a}=y$ (iii) $\frac{c+b}{c}=z$

Solving these three equations, a, b and c are found out. In this way, the atomic weights of K, Cl and Ag are determined by this method. The atomic weights of other elements are determined by this method in a similar way. The method gives accurate value of atomic weights of the elements.

Problems

Ex. 1. Calcium oxide contains 71·43 per cent of calcium. Calculate the equivalent weight of calcium.

Solution. Percentage of oxygen in calcium oxide=28·57. Hence, 28·57 parts by weight of oxygen combine with 71·43 parts by weight of calcium. Therefore, 8 parts by weight of oxygen combine with $\frac{71\cdot43\times8}{28\cdot57}=20$ parts by weight of calcium.

$\therefore$ Equivalent weight of calcium=20.

Ex. 2. The oxide of a metal contains 28·57 per cent of oxygen and the fluoride of the same metal contains 48·72 per cent of fluorine. Calculate the equivalent weight of fluorine.

Solution. 28·57 parts by weight of oxygen combine with 71·43 parts by weight of the metal. Hence, 8 parts by weight of oxygen combine with $\frac{71\cdot43\times8}{28\cdot57}=20$ parts by weight of the metal.

Therefore, the equivalent weight of the metal = 20.

Now, 51·28 parts by weight of the metal combine with 48·72 parts by weight of fluorine. Hence, 1 equivalent of the metal, i.e., 20 parts by weight of the metal combine with $\frac{48\cdot72\times20}{51\cdot28}=19$ parts by weight of fluorine.

Hence, the equivalent weight of fluorine = 19.

Ex. 3. 3·06 grams of a metal when dissolved in an acid evolved 3·34 litres of hydrogen collected over water at 27°C and 726·7 mm pressure. Calculate the equivalent weight of the metal. Aqueous tension at 27°C = 26·7 mm.

Solution. Pressure of dry hydrogen = 726·7 − 26·7 = 700 mm

Volume of hydrogen = 3·34 litres.

Temperature at which it is collected = 27 + 273 = 300°A.

Let V litres be the volume at N.T.P.

Then $\frac{760\times V}{273}=\frac{700\times3\cdot34}{300}$

or, V = 2·8 litres.

The weight of 2·8 litres of hydrogen at N.T.P.

$=2\cdot8\times0\cdot09=0\cdot252$ grams.

Therefore, 0·252 gram of hydrogen is displalced by 3·06 grams of the metal.

∴ 1·008 grams of hydrogen are displaced by $\frac{3\cdot06\times1\cdot008}{0\cdot252}=12\cdot2$ grams of metal.

Hence, the equivalent weight of the metal is 12·2.

Ex. 4. The equivalent weight of a metal is 12. What volume of hydrogen will be evolved at 27°C and 750 mm pressure when 1 gram of the metal is dissolved in dil. hydrochloric acid ?

Solution. Since 12 is the equivalent weight of the metal, we have :

12 grams of the metal will displace 1 gram of hydrogen

∴ 1 gram of the metal will displace $\frac{1}{12}$ gram of hydrogen = 0·0833 gram.

At N.T.P., 0·00009 gram of hydrogen occupies 1 c.c.

or, 0·0833 gram of hydrogen occupies $\frac{0\cdot0833}{0\cdot00009}=925$ c.c.

Hence, the volume of hydrogen evolved at N.T.P.=925 c.c.

Let V be the volume at 27°C and 750 mm pressure.

Then we have

$$\frac{750\times V}{300}=\frac{760\times 925}{273}$$

$$\text{or,}\quad V=1029 \text{ c.c.}$$

Ex. 5. 0·1458 gram of the chloride of a metal was quantitatively converted into the oxide which weighed 0·1 gram. Calculate the equivalent weight of the metal.

Solution. Let x be the equivalent weight of the metal. Then $(x+35{\cdot}5)$ grams of the metal chloride will give $(x+8)$ grams of the metal oxide, where 35·5 and 8 are the equivalent weights of chlorine and oxygen respectively. Then we have ;

$$\frac{x+35{\cdot}5}{x+8}=\frac{0{\cdot}1458}{0{\cdot}1} \text{ whence } x=52.$$

Ex. 6. The vapour density of the chloride of an element is 55·5 and the oxide of the element contains 71·43 per cent of the element. Calculate the valency and the atomic weight of the element. What is the formula of the oxide and the chloride ?

Solution. 28·57 grams of oxygen combine with 71·43 grams of the element.

8 grams of oxygen combine with $\frac{71{\cdot}43\times 8}{28{\cdot}57}=20$ grams of the element.

Hence, the equivalent weight of the element is 20.

Let the valency of the element be n.

$\therefore$ Atomic weight of the element$=20\times n$

Again, the molecular weight of the chloride$=2\times$vapour density $=2\times 55{\cdot}5=111$

Since the valency of the element is n, the molecular formula of the chloride is MCl_n since chlorine is univalent. Hence, we get

$$20\times n+35{\cdot}5\times n=111$$

$$\text{or,}\quad n=\frac{111}{55{\cdot}5}=2.$$

and atomic weight of the element$=20\times 2=40$.

The formula of the oxide is MO and that of the chloride is MCl_2.

Ex. 7. 1·56 grams of a metallic oxide were heated in a stream of hydrogen until it was completely reduced and the resulting water vapour was absorbed in previously weighed tube containing anhydrous calcium chloride. After the experiment, the increase in weight of the tube was found to be 0·36 gram. Calculate the chemical equivalent of the metal.

Solution. Since the increase in weight of the tube is due to the absorption of water by calcium chloride, we have

Weight of water formed $=0{\cdot}36$ gram

Now, 18 grams of water contain 16 grams of oxygen.

$\therefore$ Weight of oxygen combining with the metal $=\dfrac{16\times 0{\cdot}36}{18}$

$=0{\cdot}32$ gram.

$\therefore$ Weight of metal in 1·56 grams of the oxide $=1{\cdot}24$ grams.

$\therefore$ 0·32 gram of oxygen combines with 1·24 grams of the metal.

$\therefore$ 8 grams of oxygen combine with $\dfrac{1{\cdot}24\times 8}{0{\cdot}32}=31$

Hence, the equivalent weight of the metal is 31.

Ex. 8. 0·4596 gram of a metal was placed in copper sulphate solution and the displaced copper, when dry, weighed 1·2132 grams. If the equivalent weight of copper is 31·7, calculate that of the metal.

Solution. 1·2132 grams of copper are displaced by 0·4596 gram of the metal. Hence, 31·7 grams of copper are displaced by $\dfrac{0{\cdot}4596\times 31{\cdot}7}{1{\cdot}2132}=12$. Therefore, 12 is the equivalent weight of the metal.

Ex. 9. 1·48 grams of a metal (M) displace from an acid 0·6691 litre of dry hydrogen at 27°C and 740 mm pressure. The specific heat of the metal is 0·1146 cal/g. deg. Calculate the exact atomic weight of the metal. Find the formula of the oxide and chloride of the metal.

Solution. Let V litre be the volume of hydrogen at N. T. P. Then,

$$\frac{740\times 0{\cdot}6691}{300}=\frac{760\times V}{273}$$

whence $V=0{\cdot}594$ litre.

Now, 1 litre of hydrogen weighs 0·09 gram at N.T.P.

$\therefore$ 0·594 litre of hydrogen weighs $0{\cdot}09\times 0{\cdot}594=0{\cdot}05346$ gram.

Hence, 0·05346 gram of hydrogen is displaced by 1·48 grams of metal.

$\therefore$ 1·008 grams of hydrogen are displaced by $\dfrac{1{\cdot}48\times 1{\cdot}008}{0{\cdot}05346}=27{\cdot}905$ grams of metal.

Therefore, the equivalent weight of the metal is 27·905

Rough atomic weight of the metal$=\frac{6\cdot3}{0\cdot1146}=54\cdot9$

Now, valency$=\frac{\text{atomic weight}}{\text{equivalent weight}}=\frac{54\cdot9}{27\cdot9}=1\cdot96=2$, since valency of an element is a whole number.

Hence, the exact atomic weight of the metal$=27\cdot905\times2=55\cdot81$.

The formula of the oxide is MO and that of the chloride is MCl_2.

Ex. 10. On dissolution of 2 grams of a metal in sulphuric acid 2·927 grams of the metal sulphate were formed. If the specific heat of the metal is 0·031 cal/g. deg., calculate the valency of the metal and its exact atomic weight.

Solution. Since in sulphuric acid, H_2SO_4, 96 grams of sulphate radical combine with $1\cdot008\times2=2\cdot016$ grams of hydrogen, the equivalent weight of sulphate radical is $\frac{96}{2}=48$.

Weight of sulphate radical in metal sulphate$=0\cdot927$ gram

Hence, 0·927 grams of sulphate radical combine with 2 grams of metal.

$\therefore$ 48 grams of sulphate radical combine with $\frac{2\times48}{0\cdot927}=103\cdot56$ grams of metal.

Hence, the equivalent weight of the metal is 103·56

Now, approximate atomic weight of the metal$=\frac{6\cdot3}{0\cdot031}=203\cdot2$

$\therefore$ Valency of the element$=\frac{203\cdot2}{103\cdot56}=1\cdot96=2$ ($\because$ valency is a whole number.)

$\therefore$ exact atomic weight of the metal$=103\cdot56\times2=207\cdot12$.

Ex. 11. An element has a sp. ht. of 0·03. The oxide of the element contains 10% oxygen. Calculate the exact atomic weight of the element. [J. E. E., '74]

Solution. 10 parts by weight of oxygen combine with 90 parts by weight of the metal

$\therefore$ 8 parts by weight of oxygen combine with $\frac{90\times8}{10}=72$ parts by weight of the metal

$\therefore$ Equivalent weight of metal$=72$

Rough atomic weight of the metal$=\frac{6\cdot3}{0\cdot03}=210$

Now, valency$=\frac{\text{At. wt.}}{\text{Eq. wt.}}=\frac{210}{72}=2{\cdot}9=3$, since valency of an element is a whole number

$\therefore$ Exact at. wt.$=72\times3=216$.

Ex. 12. 1·878 gram of a metal bromide MBr_x when heated in a stream of hydrogen chloride gas is completely converted to the chloride MCl_x which weighs 1·000 gram. The metal M has a specific heat of 0·14 cal/g. °C. Calculate the molecular weight of the metal bromide. [I. I. T., '68]

Let the equivalent weight of the metal be e

The weight of $MCl_x=1$ gram

The weight of $MBr_x=1{\cdot}878$ gram

$\therefore\ \frac{e+35{\cdot}5}{e+80}=\frac{1}{1{\cdot}878}\qquad\therefore\ e=15{\cdot}183$

$\therefore$ The equivalent weight of $M=15{\cdot}183$

The approximate atomic weight of $M=\frac{6{\cdot}4}{0{\cdot}14}=46$

$\because$ The valency of $M=\frac{46}{15{\cdot}183}=3{\cdot}02=3$ [$\because$ valency is a whole number]

$\therefore$ Exact atomic weight of $M=15{\cdot}183\times3=45{\cdot}549$

The molecular formula of metal bromide is MBr_3

The molecular weight of metal bromide

$$=45{\cdot}549+3\times80=285{\cdot}549.$$

Ex. 13. A sample of metal chloride weighing 0·22 gram required 0·51 gram of silver nitrate to precipitate the chloride completely. The specific heat of the metal is 0·057. Find out the molecular formula of the chloride if the symbol of the metal is M.

(At. wt of Ag=108) [I. I. T., '76]

$$\frac{\text{weight of metal chloride}}{\text{weight of silver nitrate}}=\frac{\text{Equivalent weight of metal chloride}}{\text{Equivalent weight of silver nitrate}}$$

Let the equivalent weight of the metal be e

the equivalent weight of silver$=108$

$\therefore\ \frac{0{\cdot}22}{0{\cdot}51}=\frac{e+35{\cdot}5}{108+62}\ \left[\because\ \text{eq. wt. of } NO_3^-=62\right]$

$\therefore\ e=37{\cdot}83$

The approximate at. wt. of the metal$=\frac{6{\cdot}4}{0{\cdot}057}=112{\cdot}3$

∴ The valency of the metal$=\frac{112\cdot3}{37\cdot83}=2\cdot9=3$ [∵ valency is a whole number]

∴ The molecular formula of metal chloride is MCl_3.

Ex. 14. A hydrated sulphate of a metal contains 8·1% metal and 43·2% of sulphate (SO_4^{-2}) by weight. The specific heat of the metal is 0·242. Determine the formula of the sulphate of the metal. [I. I. T., '77]

Let the symbol of the metal be M

Percentage of the metal=8·1

Percentage of the sulphate=43·2

Percentage of water of crystallisation=100−(8·1+43·2)=48·7

Approximate atomic weight of the metal$=\frac{6\cdot4}{0\cdot242}=26\cdot446$

$$\text{Now, } \frac{\text{Weight of M}}{\text{Weight of } SO_4}=\frac{\text{Equivalent weight of M}}{\text{Equivalent weight of } SO_4}$$

$$\therefore \frac{8\cdot1}{43\cdot2}=\frac{\text{Equivalent weight of M}}{48}$$ [∵ equivalent weight of SO_4=48]

∴ Equivalent weight of M=9

Valency of M$=\frac{26\cdot446}{9}=3$ $\left[\because\right.$ valency is a whole number. $\left.\right]$

The exact atomic weight of M=9 × 3=27

$$\therefore \quad M : SO_4 : H_2O=\frac{8\cdot1}{27}:\frac{43\cdot2}{96}:\frac{48\cdot7}{18}=2:3:18.$$

∴ The formula of the hydrated sulphate of the metal is $M_2(SO_4)_3, 18\,H_2O$.

Ex. 15. When 2 grams of calcium carbonate are heated strongly 1·12 gram of calcium oxide is formed. Calculate the equivalent weight of calcium.

Let the equivalent weight of calcium be x

the equivalent weight of oxygen=8

the equivalent weight of $CO_3=\frac{12+3\times16}{2}=30$

$$\text{Now, } \frac{\text{weight of calcium oxide}}{\text{weight of calcium carbonate}}$$

$$=\frac{\text{equivalent weight of calcium oxide}}{\text{equivalent weight of calcium carbonate}}$$

$$\therefore \quad \frac{1{\cdot}12}{2}=\frac{x+8}{x+30} \qquad \text{or,} \quad x=20$$

∴ Equivalent weight of calcium = 20.

Ex. 16. The formula of a metal oxide is M_2O_3. The ratio of the weights of the metal (M) and oxygen in the oxide is 1·125 : 1. Determine the atomic weight and the specific heat of the metal.

$$\frac{\text{weight of the metal}}{\text{weight of oxygen}}=\frac{1{\cdot}125}{1}=\frac{9}{8}$$

Equivalent weight of oxygen = 8. Hence, the equivalent weight of the metal is 9. Now, the formula of metal oxide is M_2O_3. Hence, the velency of the metal is 3.

∴ Atomic weight of the metal = 9 × 3 = 27

$$\therefore \quad \text{Specific heat of the metal}=\frac{6{\cdot}4}{\text{Atomic weight}}=\frac{6{\cdot}4}{27}=0{\cdot}237.$$

Ex. 17. A metal chloride contains 24·7% chlorine and it is isomorphous with KCl. Determine the atomic weight of the metal.

The chloride of the metal (M) is isomorphous with KCl. Hence, the molecular formula of the chloride is MCl.

Now in MCl, the percentage of chlorine is 24·7

∴ the percentage of metal = 100 − 24·7 = 75·3

Hence 24·7 gram of chlorine combine with 75·3 gram of the metal.

Hence, 35·5 gram of chlorine combine with $\frac{75{\cdot}3\times35{\cdot}5}{24{\cdot}7}$

= 108·2 gram of metal

∴ Equivalent weight of M = 108·2

Now in KCl, the valency of K = 1

Hence in MCl, the valency of M = 1

∴ Atomic weight of M = 108·2 × 1 = 108·2.

Ex. 18. Potassium selenate (containing 35·75% selenium) is isomorphous with potassium sulphate (K_2SO_4). If the atomic weight of sulphur is 32, calculate the atomic weight of selenium.

[Bombay Inter., 1953]

The formula of potassium sulphate is K_2SO_4

Hence, the formula of potassium selenate is K_2SeO_4.

Let the atomic weight of selenium be a

∴ Mol. wt. of $K_2SeO_4=2\times39+a+4\times16=(142+a)$

Now $(142+a)$ gram of K_2SeO_4 contain a gram of selenium

∴ 100 gram of K_2SeO_4 contain $\frac{a\times100}{142+a}$ gram of selenium.

$$\therefore \frac{a \times 100}{142+a} = 35{\cdot}75$$

$$\therefore a = 79$$

∴ Atomic weight of selenium is 79.

Ex. 19. The oxides of A and B are isomorphous with one another. The atomic weight of A is 27 and the vapour density of its chloride is 66·75. If the oxide of B contains 30·06% oxygen, find the atomic weight of B.

Let us suppose that the valency of A$=n$.

∴ The formula of its chloride is ACl_n

The molecular weight of $ACl_n = 2 \times$ vapour density

$$= 2 \times 66{\cdot}75 = 133{\cdot}5$$

$\therefore\ 133{\cdot}5 = 27 + n \times 35{\cdot}5 \quad \therefore\ n = 3$

∴ The formula of the oxide of A is A_2O_3.

∴ The formula of the oxide of B is B_2O_3. Hence, the valency of B is 3.

Now, 30·06 gram of oxygen combine with $(100 - 30{\cdot}06) = 69{\cdot}94$ gram of B.

∴ 8 gram of oxygen combine with $\frac{69{\cdot}94 \times 8}{30{\cdot}06} = 18{\cdot}608$ gram of B.

∴ Equivalent weight of B$=18{\cdot}608$

∴ Atomic weight of B$=18{\cdot}608 \times 3 = 55{\cdot}824$

EXERCISES

1. Explain the meaning of the term equivalent weight. Describe an experiment to determine the equivalent weight of hydrogen.

2. Establish a relation between atomic weight, equivalent weight and valency of an element. How will you explain that the equivalent weight of an element may vary?

3. Describe experiments by which the equivalent weights of the following elements might be determined:

(i) copper, (ii) silver, (iii) potassium, and (iv) magnesium.

4. Describe in detail how an accurate determination of the equivalent weight of carbon may be carried out. Explain how the atomic weight of carbon may be derived when its equivalent weight is known.

5. Suggest methods by which the equivalent weights of the following elements may be determined:

(i) phosphorus, (ii) silicon, (iii) sulphur and (iv) bromine.

6. State Dulong and Petit's law and show how this law is used in determining the exact atomic weight of an element.

7. State Mitscherlich's law of isomorphism. Show how the law may be used in determining the atomic weight of an element.

8. State with illustrations the law of equivalent proportions. Show that the law of reciprocal proportions and the law of equivalent proportions are different forms of the same law. [J. E. E., '79]

9. Define: (a) equivalent weight and gram-equivalent weight, (b) equivalent weight of radical and (c) equivalent weight of compound.

Show that an element may have more than one equivalent weight.

10. What is the difference between equivalent weight and atomic weight of an element? Explain with examples. Under what conditions they have the same value and under what conditions they have different values? [H. S., '63]

11. What is equivalent weight of an element? Explain the relation between valency and equivalent weight. [H. S., '80]

"The equivalent weight of an element may vary"—explain with examples.

12. "Equivalent weight of calcium is 20 and its atomic weight is 40"—what do you mean by this statement?

The equivalent weight of an element is 9. What informations are necessary in order to determine its atomic weight?

13. "The equivalent weight of an element depends on the nature of reaction it undergoes"—Explain with examples.

14. Determine the equivalent weight of the elements underlined in the following reactions:

(a) $Fe+2HCl=\underline{FeCl_2}+H_2$

(b) $NaOH+\underline{H_3PO_4}=NaH_2PO_4+H_2O$

(c) $Cl_2+\underline{2KI}=2KCl+I_2$

(d) $KOH+\underline{H_2SO_4}=KHSO_4+H_2O$

(e) $2KOH+\underline{H_2SO_4}=K_2SO_4+2H_2O$

(f) $\underline{CuO}+H_2=Cu+H_2O$

(g) $\underline{NaH}+H_2O=NaOH+H_2$

(h) $\underline{2NH_3}+3Cl_2=6HCl+N_2$

(i) $4Cu+\underline{2NO_2}=4CuO+N_2$

(j) $Zn+2HCl=\underline{ZnCl_2}+H_2$

15. (a) Explain with examples the importance of Dulong and Petit's law. [H. S., '80]

(b) What is meant by isomorphism? Give examples of some isomorphous compounds. What are the criteria of isomorphism?

16. (a) How is the equivalent weight of zinc determined by hydrogen displacement method?

(b) Name the elements whose equivalent weights can be determined by hydrogen displacement method.

17. (a) Why the equivalent weight of copper cannot be determined by hydrogen displacement method?

(b) How is the equivalent weight of copper determined by oxidation method? Why is copper not converted directly into its oxide in this method?

18. Discuss with examples the principle of determination of equivalent weight of a metal by displacement of one metal by another.

19. Discuss the method for the determination of equivalent weight of sodium. Why is the compound of sodium taken instead of sodium in the determination of equivalent weight of sodium ?

20. (a) Describe a method for the determination of the equivalent weight of silver.

(b) Why is the equivalent weight of silver not determined by hydrogen displacement method or by oxide-formation method ?

21. How is the atomic weight of an element determined from the vapour density of its volatile chloride ?

22. State Mitscherlich's law of isomorphism. Explain how the atomic weight of an element is determined with the help of this law.

23. Describe how the exact atomic weight of an element is determined.

24. Explain the following :

(i) Sodium chloride and potassium chloride are not isomorphous but sodium chloride and sodium bromide are isomorphous.

(ii) In the determination of the equivalent weight of potassium, potassium compounds are taken instead of potassium.

(iii) In the determination of equivalent weight of silver, silver is not directly converted into its oxide.

(iv) Elements combine with one another in the ratio of their equivalent weights or in the ratio of the multiples of their equivalent weights.

(v) Equivalent weight of silver cannot be determined by hydrogen displacement method.

Problems

Ex. 1. 12 grams of aluminium on burning in oxygen completely, form 22·656 grams of alumina. Calculate the equivalent weight of aluminium. [Ans. 9]

Ex. 2. Silver oxide contains 93·10% silver. Calculate the equivalent weight of silver. [Ans. 107·9]

Ex. 3. The oxide of a metal contains 7·17 per cent of oxygen and the sulphide of the same metal contains 13·38 per cent of sulphur. Calculate the equivalent weight of sulphur. [Ans. 15·9]

Ex. 4. On dissolution of 0·218 grams of magnesium in hydrochloric acid, 218·2 c.c. of moist hydrogen measured at a temperature of 17°C and 754·5 mm of Hg were evolved. Calculate the equivalent weight of the metal. Aqueous tension at 17°C = 14·4 mm of Hg. [Ans. 12·24] [Patna, 1928]

Ex. 5. 7·1829 grams of a metal when dissolved in sulphuric acid evolved 2·8 litres of hydrogen measured at N.T.P. Determine the equivalent weight of the metal. [Ans. 32·7]

Ex. 6. 0·3302 gram of a metal when dissolved in hydrochloric acid evolves 122·2 c.c. of hydrogen collected over water at a temperature of 16°C and 758 mm pressure. If the atomic weight of the metal is 65·4, what is the valency of the metal ? Aqueous tension at 16°C=13·6 mm of Hg. [Ans. 2]

Ex. 7. The vapour density of the chloride of an element is 77. The oxide of the same element contains 72·72% oxygen. Calculate the valency and the atomic weight of the element. [Ans. valency 4. At. wt. 12.]

Ex. 8. In order to dissolve 1·962 grams of metal, 2·94 grams of sulphuric acid whose equivalent weight is 49 were spent. Determine the equivalent weight of the metal and the volume of hydrogen evolved during its dissolution. [Ans. 32·7 ; 0·671 litre at N.T.P.]

Ex. 9. The chloride of an element was converted quantitatively into the corresponding oxide, and the following figures were obtained : 0·1827 gram of the chloride gave 0·1057 gram of the oxide. Calculate the equivalent weight of the element (Cambridge Entrance School). [Ans. 29·74]

Ex. 10. Tin oxide contains 78·8 per cent of tin. If the specific heat of tin is 0·0556 cal/g. deg., calculate the accurate atomic weight of tin. [Ans. 118·9]

Ex. 11. 0·10595 gram of a metal combines with oxygen to form 0·13261 gram of an oxide. The specific heat of the metal is 0·0936 cal/g deg. Determine the most accurate value for the atomic weight of the metal that can be calculated from these data. [Ans. 63·57]

Ex. 12. On dissolution of 1·216 grams of a metal, 6·016 grams of sulphate were formed. The specific heat of the metal is 0·25 cal/g. deg. What is the valency of the metal and its exact atomic weight ? [Ans. 2 ; 24·32]

Ex. 13. On dissolution of 0·1 gram of a metal in hydrochloric acid, 124·4 c.c. of dry hydrogen at N.T.P. were evolved. If the specific heat of the metal is 0·214, calculate the accurate atomic weight of the metal. [Ans. 26·80] [Cal., '53]

Ex. 14. The equivalent weight of a volatile metal is 100·3. The specific heat of the metal is 0·033. 0·25 gram of the metal occupies 79·5 c c. at 500°C and 760 mm pressure. Calculate the atomic weight of the metal and the molecular weight of its vapour. [Ans. At. wt. 200·6, Mol. wt. 199·5] (Cambridge H.S.C.)

Ex. 15. What is the atomic weight of an element which has the following properties : (a) 1 gram of the element combines with 0·1713 gram of chlorine. (b) The specific heat of the element is 0·031 cal/g. deg. [Ans. 207·2]

Ex. 16. 1·17 grams of sodium chloride precipitates 2·8676 grams of silver chloride, when treated with excess of silver nitrate solution. Calculate the equivalent weight of sodium. Given eq. wt. of Ag. = 107·88, eq. wt. of Cl_2 = 35·5. [Ans. 23]

Ex. 17. Analysis of a pure metallic oxide showed it to contain 3·5 grams of the metal (M) to 1·0 gram of oxygen ; what is the equivalent weight of the metal ? The formula of its chloride is MCl_2. Calculate the approximate specific heat of the metal. [Ans. 28·0 ; 0·112]

Ex. 18. 1·538 grams of copper oxide were obtained by oxidising 1·226 grams of copper by nitric acid. When 0·383 grams of magnesium were placed in copper sulphate solution, 1·011 gram of copper was precipitated. Calculate the equivalent weight of copper and magnesium. [Ans. Cu=31·4, Mg.=12·2]

Ex. 19. 1 gram of barium chloride when treated with H_2SO_4 yields 1·119 grams of barium sulphate. Calculate the equivalent weight of barium. Given : Eq. wt. of sulphate=48. [Ans. 69·1]

Ex. 20. 2·5 grams of a pure metal carbonate when heated produce 1·4 grams of metal oxide. Calculate the equivalent weight of the metal. Given : at wt. of C=12. [Ans. 20]

[Hints. Let x be the atomic wt. of the metal ; then

$$\frac{\text{eq. wt. of metal carbonate}}{\text{eq. wt. of metal oxide}}=\frac{x+30}{x+8}=\frac{2\cdot5}{1\cdot4} \text{ whence, } x=20$$

for eq. wt. of $CO_3=\frac{12+48}{2}=30$ and eq. wt. of oxygen=8]

Ex. 21. The chloride of a metal M contains 20·2 per cent of the metal. What is the accurate atomic weight of the metal, if its specific heat is 0·224 cal/g. deg. The relative density of the chloride is 66·7. Derive its molecular formula.

[Ans. at. wt. 26·9, MCl_3.] [Punjab, '51]

Ex. 22. An oxide of an element contains 53·33% oxygen and the chloride of the same element contains 83·5% of chlorine. 100 c.c. of the chloride weigh 0·759 gram at N.T.P. The specific heat of the element is 0·17 cal/g. deg. Calculate the equivalent weight and atomic weight of the element. Derive the formula of the chloride. [Ans. eq. wt.=6·94, at wt.=28, MCl_4]

Ex. 23. Two salts each containing only potassium, oxygen and one other element, were found to be isomorphous. One contained 28·2 per cent of potassium and 25·6 per cent of chlorine, the other contained 24·7 per cent of potassium and 34·8 per cent of manganese. What value for the atomic weight of manganese is indicated by these data ? [Ans. 55·09] [Cambridge. H. S. C.]

Ex. 24. Calcium carbonate is isomorphous with magnesium carbonate. Calcium carbonate contains 40·06% Ca, 11·99% C and 47·95% oxygen. Magnesium carbonate contains 28·91% Mg, 14·22% carbon and 56·87% oxygen. If the atomic weight of calcium is 40·1, find the atomic weight of magnesium. [Ans. 24·40]

Ex. 25. Ferric oxide is isomorphous with aluminium oxide Al_2O_3. The per cent of oxygen in ferric oxide and aluminium oxide

is 30·06 and 47·06 respectively. If the atomic weight of alum
is 27, find the atomic weight of iron.

Solution. In ferric oxide, 30·06 grams of oxygen combine with 69·94 grams of iron.

In aluminium oxide, 47·06 grams of oxygen combine with 52·94
grams of aluminium.

or, 30·06 grams of oxygen combine with $\frac{52\cdot94\times30\cdot06}{47\cdot06}=3$

grams of aluminium.

Let x be the atomic weight of iron, then by the law of isomo
phism.

$$\frac{69\cdot94}{x}=\frac{33\cdot78}{27} \text{ whence } x=55\cdot89.$$

Ex. 26. Ferrous sulphate, $FeSO_4$, $7H_2O$, is isomorphous with
zinc sulphate. Ferrous sulphate contains 20·09% of Fe and 45·3
of water and zinc sulphate contains 22·7% of Zn and 43·8% o
water. If the atomic weight of iron is 55·84, find that of zinc.

Solution. The formula of zinc sulphate is, therefore, ZnSO
$7H_2O$. In ferrous sulphate, 20·09 grams of iron combine with 34·6
grams of sulphate radical.

In zinc sulphate, 22·7 grams of Zn combine with 33·5 grams
sulphate radical.

Hence, 34·61 grams of sulphate combine with 23·42 grams of zinc.

Let x be the atomic weight of Zn, then by the law of isomorphism.

$$\frac{20\cdot09}{55\cdot84}=\frac{23\cdot42}{x} \text{ whence } x=65\cdot11.$$

Ex. 27. Potassium sulphate K_2SO_4 (containing 18·3% sulphur) and potassium chromate (containing 26·8% chromium) are isomorphous. If the atomic weight of sulphur is 32, find that of chromium.

Solution. In potassium sulphate, 18·3 grams of sulphur are in combination with 81·7 grams of potassium and oxygen. Hence, 1 gram of potassim and oxygen together combine with $\frac{18\cdot3}{81\cdot7}=0\cdot2239$ gram of sulphur. In potassium chromate, 26·8 grams of chromium combine with 73·2 grams of potassium and oxygen. Therefore, 1 gram of potassium and oxygen together combine with $\frac{26\cdot8}{73\cdot2}=0\cdot3661$ gram of chromium. Let x be the atomic weight of chromium, then we have

$$\frac{x}{32}=\frac{0\cdot3661}{0\cdot2239} \text{ where } x=52\cdot3.$$

Ex. 28. Potassium selenate (containing 35·75% selenium) is isomorphous with potassium sulphate (containing 18·39% sulphur). If the atomic weight of sulphur is 32, calculate the atomic weight of selenium. [Ans. 79] [Bombay Inter., 1953]

Ex. 29. 2 grams of a metal when dissolved in sulphuric acid 4·51 gram of metal sulphate was formed. The specific heat of the metal is 0·057 cal/gram. Calculate the valency and exact atomic weight of the metal. [Ans. 115·2, 3] [I. I. T., '78]

Ex. 30. The specific heat of an element is 0·03. The oxide of the metal contains 10% oxygen. Calculate the exact atomic weight of the metal. [Ans. 216] [J. E. E., '74]

Ex. 31. 1·6182 gram of pure silver is dissolved in nitric acid. To this solution excess of hydrochloric acid is added when 2·1501 gram of silver chloride is precipitated. If the equivalent weight of chlorine is 35·5, what is the equivalent weight of silver ?
[Ans. 107·92] [H. S. '65]

Ex. 32. 0·3975 gram of cupric oxide is heated in a current of pure and dry hydrogen until it is completely reduced to metallic copper. The liberated gaseous compound is passed through previously weighed calcium chloride tube. If the increase in weight of calcium chloride tube is 0·09 gram, calculate the equivalent weight of copper. [Ans. 31·75] [H. S., '64]

Ex. 33. 0·6842 gram of copper is dissolved in nitric acid. The resulting solution is evaporated to dryness. The solid residue on being heated gives 0·8567 gram of cupric oxide. Calculate the equivalent weight of copper. [Ans. 31·728] [H.S. (Comp.), '60]

Ex. 34. The equivalent weights of magnesium and oxygen are respectively 12 and 8. Calculate the percentage amount of magnesium in magnesium oxide. [Ans. 60]

Ex. 35. 2·470 gram of CuO is obtained from 1·986 gram of copper. When 0·346 gram of zinc is added to copper sulphate solution 0·335 gram of copper is displaced. What is the equivalent weight of zinc ? [Ans. 33·808] [H. S., '81]

Ex. 36. 1·02 gram of a metal oxide contains 0·54 gram of the metal. What is the equivalent weight of the metal ? Calculate the atomic weight of the metal by Dulong-Petit's law. Taking M as symbol of the metal, determine the molecular formula of the metal oxide. [The specific heat of the metal is 0·216/gram. deg.]
[Ans. 9, M_2O_3] [H. S., '82]

Ex 37. 1·5276 gram of $CdCl_2$ contain 0·9367 gram of cadmium. Calculate the atomic weight of cadmium. At. wt. of chlorine is 35·5. [Ans. 112·535] [I. I. T., '75]

Ex. 38. The specific heat of an element is 0·031 cal. per gram per deg. It was found that 25·9 gram of the element combines with 4·0 gram of oxygen. Calculate the atomic weight of the element. [Ans. 207·2] [I. I. T., '66]

Ex. 39. A sample of metal oxide weighing 6·5 gram is decomposed quantitatively to give 6·251 gram of the metal. The specific heat of the metal is 0·0332 cal./gram. Calculate the exact atomic weight of the metal and the empirical formula of the oxide.
[Ans. 200·8 ; M_2O] [I. I. T., '69]

Ex. 40. What is the valency of an element of which the equivalent weight is 12 and the specific heat is 0·25 ?
[Ans. 2] [I. I. T., '71]

Ex. 41. The equivalent weight of an element is 12·2. Calculate the amount of the metal required to produce and collect by the displacement of water 3·34 litre of hydrogen at 27°C and 726·7 mm. pressure. Aqueous tension=26·7 mm. Hg. 1 litre of hydrogen weighs 0·09 gram at N. T. P. [Ans. 3·06 gram]

Ex. 42. 0·1 gram of a metal carbonate reacts with sulphuric acid to produce 0·136 gram of metal sulphate. Calculate the equivalent weight of the metal. [Ans. 20.]

Ex. 43. The chloride of an element contains 16·47% element. The molecular weight of the chloride is 170. Calculate the atomic weight of the element and determine its valency.
[Ans. 28 ; 4]

Ex. 44. The oxide of an element (M) contains 72·72% oxygen. The vapour density (O=1) of the chloride of the element is 4·82. Calculate the atomic weight of the element and determine the formula of the chloride. [Ans. 12, MCl_4.]

Ex. 45. In order to precipitate chlorine completely from 0·585 gram of a metal chloride 1·70 gram of silver nitrate were required. If the specific heat of the metal is 0·28, calculate the equivalent weight, atomic weight and valency of the metal.
[Ans. Eq. wt.=23, valency=1, at. wt.=23.]

Ex. 46. 0·51 gram of silver nitrate is required to precipitate chlorine from 0·1335 gram of a metal chloride. The specific heat of the metal is 0·22. Calculate the equivalent weight, atomic weight and valency of the metal. [Ans. 9, 27, 3]

Ex. 47. 1·56 gram of a liquid chloride of phosphorus is hydrolysed. When silver nitrate was added to the resulting solution, silver chloride is precipitated. Silver chloride was filtered, washed and dried. The weight of dry silver chloride was found to be 4·883 gram. If the equivalent weight of silver and chlorine are respectively 107·9 and 35·45, calculate the equivalent weight of phosphorus. [Ans. 10·34] [London Inter.]

Ex. 48. 2·71 grams of ferric chloride react with 2 grams of sodium hydroxide leaving no residue. If the equivalent weight of NaOH is 40, find the equivalent weight of ferric chloride.
[Ans. 54·2]

Ex. 49. Potassium permanganate is isomorphous with potassium perchlorate ($KClO_4$). If 34·81% of Mn is present in potassium permanganate, calculate the atomic weight of manganese. [Ans. 55]

Ex. 50. Potassium manganate K_2MnO_4 is isomorphous with potassium chromate. If potassium chromate contains 26·8% chromium, calculate the atomic weight of chromium. K=39, O=16 [Ans. 52]

Ex. 51. A metal chloride contains 52·5% metal and it is isomorphous with silver chloride. If siver chloride contains 24·8% silver, calculate the atomic weight of the metal. Ag=108. [Ans. 39·3]

Ex. 52. The chloride of a metal (M) contains 29·34% chlorine and it is isomorphous with KCl. Calculate the atomic weight of the metal. [Ans. 85·5] [C. U., '38]

Ex. 53. Cu_2S and Ag_2S are isomorphous with one another. Cu_2S and Ag_2S contain 20·14% and 12·94% sulphur respectively. If the atomic weight of silver is 107·9, calculate the atomic weight of copper. [Ans. 63·5]

Ex. 54. The oxides of the two metals A and B are isomorphous. The atomic weight of A is 56 and the vapour density of its chloride is 81·25. If the oxide of the metal B contain 47·1% oxygen, what is the atomic weight of B ? [Ans. 27]

Ex. 55. The sulphate of a metal (M) contains 22·6% metal and it is isomorphous with $MgSO_4$, $7H_2O$. Determine the atomic weight of the metal. [Ans. 64·82]

Ex. 56. The sulphate of a metal (M) is isomorphous with $MgSO_4$, $7H_2O$. 0·325 gram of the metal displace 1·08 gram of silver from silver nitrate solution. Determine the atomic weight of the metal. Given that the atomic weight of silver is 108 and its valency is 1. [Ans. 65]

Ex. 57. Ferrous sulphate contains 20·14% iron and 35·4% sulphate and zinc sulphate contains 22·6% zinc and 35·5% sulphate. It ferrous sulphate and zinc sulphate are isomorphous and the atomic weight of zinc is 65, calculate the atomic weight of iron. [Ans. 56·16]

Ex. 58. 1·02 gram of a metal oxide on reduction gives 0·54 gram of the metal. The sulphate of the metal forms double salt with K_2SO_4 which is isomorphous with chrome alum K_2SO_4, $Cr_2(SO_4)_3$, $24H_2O$. Determine the atomic weight of the metal. [Ans. 27]

Ex. 59. 0·152 gram of chromium oxide is formed from 0·104 gram of chromium. Its sulphate forms a double salt with potassium sulphate which is isomorphous with potash alum, K_2SO_4, $Al_2(SO_4)_3$,

$24H_2O$. If the atomic weight of aluminium is 27, what is the atomic weight of chromium. [Ans. 52·08]

Ex. 60. Determine the atomic weight of chlorine from the following data :

(i) $KClO_3$ contains 39·19% oxygen.

(ii) 100 gram of silver is precipitated by 69·1 gram of KCl.

(iii) 100 gram of silver is obtained from 132·85 gram of silver chloride. [Ans. 35·41]

Ex. 61. When 0·84 gram of a metal carbonate is heated 246·2 c.c. of carbon dioxide is obtained at 27°C and 760 mm pressure. Calculate the equivalent weight of metal. [Ans. 11·8]

Ex. 62. When lead is converted into lead sulphate, it is found that $Pb : PbSO_4 = 1 : 1{\cdot}463$. If the atomic weight of sulphur is 32, what is the atomic weight of lead ? [Ans. 207·34]

Appendix

Specific heat of elements

Definition. The specific heat of an element is defined as the quantity of heat in calories required to raise the temperature of 1 gram of the element by one degree centigrade.

It follows from the definition that the unit of specific heat is calorie per gram per degree. Since 1 calorie of heat is required to raise the temperature of 1 gram of water by 1°C, the specific heat of water is 1 calorie/gram. degree.

The quantity of heat q given up or absorbed by any substance due to a change in its temperature is given by

$q = s \times m \times t$ where s = the specific heat of the substance,

m = the mass of the substance and

t = rise in temperature in degree centigrade.

From the above equation, it follows that if m, q and t are known, s can be found out.

Therefore, by introducing a known quantity of heat into a known mass of a substance and measuring the temperature rise thereby produced, the specific heat of a substance can be determined.

Specific heats of some elements

Element	Atomic weight	Specific heat	Sp. ht. × Atomic wt.
Aluminium	26·97	0·217	5·9
Boron	10·82	0·307	3·3
Beryllium	9·02	0·43	3·8
Carbon, graphite, diamond	12	0·16	1·92
Copper	63·54	0·093	5·9
Gold	197·2	0·032	6·3
Iron	55·84	0·11	6·1
Lithium	6·94	0·9063	6·29
Lead	207·2	0·031	6·4
Mercury	200·6	0·033	6·7
Magnesium	24·32	0·25	6·1
Phosphorus (white)	31	0·198	6·2
Sodium	23·00	0·2829	6·51
Silver	107·88	0·059	6·36
Silicon	28·06	0·17	4·8
Sulphur	32	0·175	5·6
Tin	118·7	0·05	5·9
Tungsten	184·0	0·033	6·1
Thorium	232·1	0·026	6·0
Uranium	238·14	0·028	6·67
Zinc	65·5	0·094	6·2

CHAPTER VII

THE CLASSIFICATION OF COMPOUNDS

7.1. Introduction. At present, more than a million compounds are known. It would be impossible for one person to learn the chemistry of such large number of compounds if a systematic classification is not made. Just as elements are classified according to their properties in the periodic table, so compounds can be classified into several classes. Compounds in the same class have many properties in common. Four important classes of compounds, viz., acid, base, salt, and oxide will be discussed in the present chapter.

Acids. The early chemists observed that several compounds when dissolved in water give solutions which possess quite similar properties. Some of the common properties they shared are :

(a) They have a sour taste. (b) They corrode many substances, e.g., concentrated sulphuric acid attacks paper and cloths. (c) They turn blue litmus red—when a few drops of blue litmus solution are added to a solution of an acid contained in a test tube, the whole solution turns red. (d) They dissolve certain metals with the evolution of hydrogen, e.g., hydrogen can be prepared by the reaction of dilute sulphuric acid with zinc. (e) They react with bases. In this reaction, they lose all their characteristic properties and neutral salts are formed. (f) The solutions obtained when they are dissolved in water are good conductors of electric current.

Compounds which exhibit most of these properties were termed acids. All these properties of acids, however, are manifested only in aqueous solution. For example, dry hydrogen chloride HCl does not behave as an acid and even does not turn blue litmus red ; but the solution of hydrogen chloride in water is one of the most typical acids and exhibits all the properties listed above. Similarly, anhydrous sulphuric acid does not react with zinc at ordinary temperature but its solution in water reacts vigorously with zinc, liberating hydrogen.

Of the properties of acid listed above, the most important one is the ability of the acids to react with bases to form salts. All but the very weakest acids will neutralise strong bases in order to produce salts. A satisfactory definition of the acid is based on the part which they play in the formation of salts : *An acid is a compound containing one or more replaceable hydrogen atoms which can be displaced either partly or wholly by a metal to form a salt.*

Thus, the compound H_2SO_4 known as sulphuric acid contains two hydrogen atoms which can be displaced by a metal like zinc to form the salt, zinc sulphate, $ZnSO_4$.

$$H_2SO_4+Zn=H_2+ZnSO_4$$

Hence, sulphuric acid is an acid. Some examples of acids are: hydrochloric acid, HCl (hydrogen chloride), hydrobromic acid, HBr (hydrogen bromide), nitric acid, HNO_3, perchloric acid, $HClO_4$ and phosphoric acid H_3PO_4.

If we subtract one or several hydrogen atoms from a molecule of an acid displaceable an atom or a group of atoms will remain, which is called *the acid radical. Acid radicals participate in chemical reactions as a whole unit.* Thus, hydrochloric acid gives the acid radical Cl^-; sulphuric acid gives two acid radicals, viz., HSO_4^- and SO_4^{--}; phosphoric acid, H_3PO_4, gives three acid radicals $H_2PO_4^-$, HPO_4^{--} and PO_4^{---}.

7.2. Classification of acids. Acids are classed as hydracids and oxyacids. The acids which contain hydrogen and other non-metallic element or elements but not oxygen are called hydracids. Examples are hydrochloric acid, HCl, hydrobromic acid, HBr, hydrosulphuric acid, H_2S.

The acids which contain hydrogen, oxygen and another element are called oxyacids. Examples of oxyacids are sulphuric acid, H_2SO_4, phosphoric acid, H_3PO_4, nitric acid, HNO_3, etc. Oxyacids are formed from acidic oxides, e.g., $P_2O_5 + 3H_2O = 2H_3PO_4$.

Acids can be distinguished as monobasic, dibasic, tribasic, etc., by the number of hydrogen atoms in a molecule that can be replaced by metals. Thus, an acid, the molecule of which contains only one replaceable hydrogen atom that can be replaced by metals to form salts is called a monobasic acid. The monobasic acids can form only one class of salts. For example, hydrochloric acid is a monobasic acid and it forms only one class of salts, viz., chlorides:

$$Zn + 2HCl = ZnCl_2 + H_2$$
$$Ca(OH)_2 + 2HCl = CaCl_2 + 2H_2O$$
$$MgO + 2HCl = MgCl_2 + H_2O$$

A molecule of a dibasic acid contains two hydrogen atoms that can be replaced by metals. A dibasic acid forms two classes of salts. For example, sulphuric acid, H_2SO_4, is dibasic Either one atom of hydrogen can be replaced by a metal to form one class of salts known as acid salts or both atoms can be replaced to form another class of salts known as normal salts.

$$H_2SO_4 + NaOH = NaHSO_4 + H_2O$$
$$H_2SO_4 + 2NaOH = Na_2SO_4 + 2H_2O$$

7.3. Nomenclature of acids. In order to name a hydracid, one places the prefix "hydro" before the name of the identifying non-metal and the suffix "ic" is attached to the stem of the latter. Thus, hydrochloric acid, HCl, is named as:

hydro + stem of chlorine + ic = hydro + chlor + ic = hydrochloric.

The other hydracids may be similarly named. Thus, we have :

HF	HCl	HBr
Hydrofluoric acid (hydrogen fluoride)	Hydrochloric acid (hydrogen chloride)	Hydrobromic acid (hydrogen bromide)
HI	H_2S	HCN
Hydriodic acid (hydrogen iodide)	Hydrosulphuric acid (hydrogen sulphide)	Hydrocyanic acid (hydrogen cyanide)

The names in parentheses are preferred for these substances when they are in the gaseous state and the other names are preferred for their solutions in water.

Oxyacids are named by attaching 'ous' and 'ic' as suffixes to the stem of the non-metal which identifies the acid. The ending "-ic" and "-ous" are used to distinguish the acids containing more or less oxygen.

Examples are :

Sulphuric acid $H_2SO_4(+6)$
(Sulphur + ic)
Sulphurous acid $H_2SO_3(+4)$
(Sulphur + ous)

Phosphorous acid, $H_3PO_3(+3)$
Phosphoric acid, $H_3PO_4(+5)$
Nitric acid $HNO_3(+5)$
Nitrous acid $HNO_2(+3)$

The numbers in the parentheses represent the oxidation state of the identifying non-metallic element. It is found that in the "ic" acid, the identifying non-metallic element is in a state of higher oxidation than in the "-ous" acid.

When an element forms more than two oxyacids, the prefixes "hypo" and "per" are used in order to name them further. An oxyacid which contains less number of oxygen atoms than the "-ous" acid, is named by putting the prefix "-hypo" before the name of the "-ous" acid. The oxyacids having the greater number of oxygen atoms than the "-ic" acid, are named by putting the prefix "-per" before the name of the "-ic" acids. Thus, we get

Chlorous acid $HClO_2$ $(+3)$
Hypochlorous acid $HClO$ $(+1)$

Chloric acid $HClO_3$ $(+5)$
Perchloric acid $HClO_4$ $(+7)$

Mineral acids. The mineral acids which are often used in the laboratory are sulphuric acid, hydrochloric acid, and nitric acid. These acids can be derived from mineral substances.

7.4. Properties of acids from the point of view of the ionic theory. According to the Arrhenius' ionic theory, all acids when dissolved in water furnish hydrogen ion, H^+, or proton by a process of reversible ionisation. Thus :

$$HCl \rightleftharpoons H^+ + Cl^- \; ; \; HNO_3 \rightleftharpoons H^+ + NO_3^-$$

$$H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{--} \; ; \; HCN \rightleftharpoons H^+ + CN^-$$

All the properties common to aqueous solution of acids are then attributed to hydrogen ions. It is they that turn blue litmus paper red, conduct electricity in solutions, react with metals, account for the sour taste of acids, etc. All the characteristic properties of the acid are lost, if the hydrogen ion is removed by a process such as neutralisation. Therefore, according to the ionic theory, an acid is defined as follows : *An acid is a hydrogen-containing compound which ionises on solution in water to produce hydrogen ion and yields no other positively charged ions.* An acid is, therefore, regarded as a proton donor.

All the hydrogen atoms present in a molecule of an acid may not be ionised. For example, hypophosphorous acid contains three hydrogen atoms in its molecule. But it gives only one proton on ionisation :

$$H_3PO_2 \rightleftharpoons H^+ + H_2PO_2^-$$

Out of four hydrogen atoms present in a molecule of acetic acid only one hydrogen atom is ionised :

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

Metals displace only those hydrogen atoms in the molecule of acid which are ionised in solution :

$$H_3PO_2 + NaOH = NaH_2PO_2 + H_2O$$
$$CH_3COOH + KOH = CH_3COOK + H_2O$$

7.5. Strength of acids. Since the acidic properties of the acids are due to free hydrogen ions, the greater is the concentration of these ions, the stronger will be the acids. Therefore, if we compare two monobasic acids at a given dilution and find that one is half ionised and the other is two-third ionised, we say that the latter is stronger, since it yields greater number of hydrogen ions. Thus, the acids which are strongly ionised in solution yielding large concentrations of hydrogen ions are known as strong acids, while those which are weakly ionised in solution yielding low concentrations of hydrogen ions are called weak acids. Thus, *the measure of the strength of the acid is their degree of ionisation, i.e., the extent to which an acid is ionised in solution* Examples of strong acids are hydrochloric acid, sulphuric acid and nitric acids which are probably completely ionised in solution. On the other hand, acids such as acetic acid, boric acid, carbonic acid and hydrocyanic acid are weak acids because they have very low degree of ionisation.

The basicity of an acid is its ability of neutralising a base. It is measured by the number of atoms of hydrogen in one molecule of an acid which are replaceable by a metal. According to ionic theory, the basicity of an acid is defined as *the number of hydrogen ions that are formed on ionisation of one molecule of an acid in solution.* Thus, one molecule of hydrochloric acid gives one hydrogen ion or proton in solution. Hence, hydrochloric acid is monobasic or monoprotic. Sulphuric acid giving two hydrogen ions per molecule is dibasic or diprotic and so on. Acids which give more than one hydrogen ion per molecule are called polybasic or polyprotic. A polyprotic acid may ionise in several stages. Thus, the ionisation of phosphoric acid may be represented as :

(i) $H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+$
(ii) $H_2PO_4^- \rightleftharpoons HPO_4^{--} + H^+$
(iii) $HPO_4^{--} \rightleftharpoons PO_4^{---} + H^+$

7.6. **Bases and Alkalis.** There is another class of compounds which is opposite to acids. This class of compounds is known as base. Aqueous solutions of bases possess several common properties :

(i) They have a peculiar soapy feel. (ii) They taste bitter. (iii) They turn red litmus blue. (iv) They react with acids to form salt. (v) They are good conductors of electric current.

The most important properties of a base, among these, are (i) its ability to react with acids and (ii) its ability to turn red litmus blue. On the basis of these properties, a base can be defined as :

A base is a substance which reacts with an acid to give a salt and water only. Bases are generally metallic oxides and metallic hydroxides. For instance, calcium oxide reacts with hydrochloric acid to produce calcium chloride and water :

$$CaO + 2HCl = CaCl_2 + H_2O$$

Cupric oxide reacts with sulphuric acid to give copper sulphate and water :

$$CuO + H_2SO_4 = CuSO_4 + H_2O$$

Sodium hydroxide reacts with sulphuric acid to produce sodium sulphate and water :

$$2NaOH + H_2SO_4 = Na_2SO_4 + 2H_2O$$

Ferric oxide reacts with hydrochloric acid to give ferric chloride and water :

$$Fe_2O_3 + 6HCl = 2FeCl_3 + 3H_2O$$

Hence, calcium oxide, cupric oxide, sodium hydroxide and ferric oxide are all bases.

Compounds containing metals combined with hydroxyl radicals are known as *hydroxides*. Metallic hydroxides also dissolve in acids with the formation of salts and water only ; they are, therefore, bases. Thus, ferric hydroxide and zinc hydroxide react with hydrochloric acid to form the corresponding chlorides, water and no other products :

$$Fe(OH)_3 + 3HCl = FeCl_3 + 3H_2O$$
$$Zn(OH)_2 + 2HCl = ZnCl_2 + 2H_2O$$

Similarly, sodium hydroxide and potassium hydroxide react with hydrochloric acid to form the corresponding chlorides and water only :

$$NaOH + HCl = NaCl + H_2O$$
$$KOH + HCl = KCl + H_2O$$

The hydroxides of sodium and potassium are soluble in water while those of iron and zinc are insoluble. The bases which are soluble in water are known as *alkalis*. Alkalis are, generally, the hydroxides of metals. The hydroxides of sodium and potassium being soluble in water are, therefore, alkalis while the insoluble hydroxides such as ferric hydroxide, $Fe(OH)_3$, and aluminium hydroxide, $Al(OH)_3$ are not alkalis but they are bases. Therefore, *all alkalis are bases but all bases are not alkalis.*

7.7. Ionic theory of bases. According to Arrhenius' ionic theory, bases are substances which yield OH^- ion when dissolved in water. Thus, sodium hydroxide when dissolved in water undergoes the following ionisation :

$$NaOH \rightleftharpoons Na^+ + OH^-$$

A base is a substance which ionises in aqueous solution furnishing hydroxyl ion. A base can accept protons from an acid.

The basic properties of the bases are due to free hydroxyl ion, OH^-, the greater the concentration of these ions, the stronger will be the bases. The strength of a base, therefore, depends on the concentration of hydroxyl ions and hence on the degree of ionisation.

The acidity of a base is its ability to neutralise an acid and is measured by the number of hydroxyl ions produced by the ionisation of a molecule of the base. That is, it is measured by the number of protons which a molecule of a base can accept from an acid. Thus, sodium hydroxide is monoacid because one molecule of sodium hydroxide gives one hydroxyl ion on ionisation :

$$NaOH \rightleftharpoons Na^+ + OH^-$$

One molecule of barium hydroxide furnishes two hydroxyl ions on ionisation and hence it is a diacid base :

$$Ba(OH)_2 \rightleftharpoons Ba^{++} + 2OH^-$$

Similarly, ferric hydroxide, $Fe(OH)_3$ is a triacid base.

The definitions of acids and bases given above from the point of view of Arrhenius theory (classical theory) of electrolytic dissociation are applicable only to aqueous solutions. Although these definitions served a useful purpose, Chemists soon came to recognise that acid-base relationships are more general in character than Arrhenius ever suspected. For example, aqueous solutions of sodium carbonate, sodium cyanide and sodium acetate affect indicators in the same way that metallic hydroxides such as sodium hydroxide do. Many compounds which do not contain hydroxyl radicals also neutralise acids. Gaseous HCl combines with gaseous ammonia to form ammonium chloride. These and similar considerations led Bronsted and Lowry to propose a new theory called the proton theory of acids and bases. According to this theory acids and bases are defined as follows :

An acid is a substance which can donate a proton.

A base is a substance which can accept a proton.

These definitions of acids and bases can be illustrated by the following example :

The reaction between hydrogen chloride and ammonia in the gaseous state can be represented by the following equation :

$$NH_3 + HCl \rightleftharpoons \overset{+}{NH_4} + \overset{-}{Cl}$$

The proton, H^+ is donated by HCl to NH_3. Hence, HCl is an acid and NH_3 is a base.

The strength of an acid is measured by its tendency to donate protons. The strength of a base is measured by its tendency to accept protons. A strong base holds a proton tightly. Hence, the strength of a hydracid depends on the weakness of the covalent bond between the proton and the conjugate base. The weaker the covalent bond between the proton and the conjugate base the stronger is the acid. HCN is a weak acid and hence its conjugate base CN^- ion is a strong base.

7.8. Salts. *A salt is a compound obtained when all or part of the hydrogen of an acid are replaced by a metal.* Thus, when the hydrogen atom of hydrochloric acid is replaced by the metal, zinc, we get the salt, zinc chloride.

$$2HCl + Zn = ZnCl_2 + H_2$$

Similarly, calcium sulphate, $CaSO_4$, is a salt, since it is obtained from H_2SO_4 by replacing two atoms of hydrogen by one calcium atom.

7.9. Nomenclature of salts. Salts are named after the names of the acids to which they are related. If a salt contains two elements only, its name consits of the name of the metal, the stem of the name of the non-metal, and the suffix-"ide". For example, $CaCl_2$, is named as :

calcium + chlor + ide = calcium chloride.

Thus, we get :

Hydracid	Salt
Hydrochloric acid, HCl	Barium chloride, $BaCl_2$
Hydrosulphuric acid, H_2S	Cadmium sulphide, CdS
Hydrocyanic acid, HCN	Potassium cyanide, KCN

The naming of the salts which are derived from the oxyacids is made according to the following rule :

(i) If the name of the acid ends in "ic" the names of the salts end with the suffix "ate". Examples are :

Acid	Salt
Sulphuric acid, H_2SO_4	Sodium sulphate, Na_2SO_4
Nitric acid, HNO_3	Sodium nitrate, $NaNO_3$
Phosphoric acid, H_3PO_4	Sodium phosphate, Na_3PO_4

(ii) If the name of the acid ends in "-ous", the name of the salt ends in "-ite". Examples are :

Acid	Salt
Sulphurous acid, H_2SO_3	Sodium sulphite, Na_2SO_3
Nitrous acid, HNO_2	Sodium nitrite, $NaNO_2$

(iii) If the name of the acid ends in *-ic* or *-ous* and has prefix such as *per* - or *hypo* -, then the prefix *per* - or *hypo* - is retained in the name of the salt. Examples are :

Acid	Salt
Perchloric acid, $HClO_4$	Sodium perchlorate, $NaClO_4$
Periodic acid HIO_4	Sodium periodate. $NaIO_4$
Hypochlorous acid, HClO	Sodium hypochlorite, NaClO.

(iv) If a salt is formed by partial replacement of hydrogen of an acid and hence still contains replaceable hydrogen, then its name consists of the name of both metal and hydrogen. Examples are

Acid	Salt
Sulphuric acid, H_2SO_4	Sodium hydrogen sulphate, or sodium bisulphate, $NaHSO_4$
Carbonic acid, H_2CO_3	Sodium hydrogen carbonate or sodium bicarbonate, $NaHCO_3$
Phosphoric acid, H_3PO_4	Disodium hydrogen phosphate Na_2HPO_4.

7.10. Ionic theory of salts. According to ionic theory, *salts may be defined as compounds which ionise on solution in water to form positive ions other than hydrogen ion and negative ions other than hydroxyl ion.* Thus, sodium chloride when dissolved in water ionises into positively charged sodium ion, Na^+ and negatively charged chloride ion, Cl^- :

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

Similarly, we get,

$$ZnSO_4 \rightleftharpoons Zn^{++} + SO_4^{--}$$
$$NaNO_3 \rightleftharpoons Na^+ + NO_3^-$$

Salts possess no common properties because there are no ions common to aqueous solutions of all salts.

All aqueous solutions of salts are excellent conductors of electric current ; this is due to the fact that all salts are highly ionised in solution. Salts also conduct electric current in the fused state.

Salts are usually solids, and characterised by quite high melting and boiling point.

7.11. Classification of salts. Salts are usually grouped into three classes :

(i) **Acid salts.** When only part of the replaceable hydrogen atoms of a polyprotic or polybasic acid has been replaced by a metal, we obtain salts which are known as acid salts.

$$NaOH+H_2SO_4=NaHSO_4+H_2O$$

The salt $NaHSO_4$ is an acid salt since it contains hydrogen atom capable of becoming hydrogen ion in solution.

$$NaHSO_4 \rightleftharpoons Na^+ + HSO_4^- \rightleftharpoons Na^+ + H^+ + SO_4^{-2}$$

The H^+ ion can be neutralised by adding more NaOH.

$$Na\overline{OH+H}|NaSO_4=Na_2SO_4+H_2O$$

Hence, the acid salts have the properties of both salts and acids.

Examples are sodium hydrogen carbonate $NaHCO_3$, sodium dihydrogen phosphate NaH_2PO_4, and disodium hydrogen phosphate Na_2HPO_4.

(ii) **Normal salts.** *When all the replaceable hydrogen atoms of an acid are replaced by a metal, we get salts known as normal salts.* Thus, sodium sulphate, Na_2SO_4, sodium phosphate, Na_3PO_4, sodium chloride NaCl, sodium chlorate, $NaClO_3$ and sodium carbonate, Na_2CO_3, are all normal salts.

(iii) **Basic salts.** When only part of the hydroxyl radical, OH, of a polyacid or polyhydroxyl bases are replaced by a non-metal or acid radical, we obtain salts which are known as basic salts. Thus,

$$Ca(OH)_2+HCl=Ca(OH)Cl+H_2O$$
$$Pb(OH)_2+HCl=Pb(OH)Cl+H_2O$$

Calcium hydroxychloride, Ca(OH Cl, lead hydroxychloride or basic lead chloride, Pb(OH)Cl, are basic salts.

Basic salts yield OH^- ions in water solution and may be neutralised to form the normal salts.

$$Pb(OH)Cl+HCl=PbCl_2+H_2O$$

Hence, the basic salts have the properties of both salt and bases.

7.12. **Double salts.** A double salt is a mixed salt which has got an individuality of its own in the solid state but exhibit only the properties of its simpler component salts in solution. For example, K_2SO_4, $Al_2(SO_4)_3$, $24H_2O$ known as potash alum is a double salt which is prepared by dissolving potassium sulphate and aluminium sulphate in equimolecular proportions in water and allowing the solution to evaporate. It is obtained in the form of beautiful transparent crystals. It retains its own characteristics only in the solid state When dissolved in water, it acts like a mixture of K_2SO_4 and $Al_2(SO_4)_3$, from which it is prepared. Double salts conform to the law of constant proportions. They owe their existence to the similarity in size and attractive forces of two different ions. The ionisation of potash alum in water yields the ions K^+, Al^{+3} and SO_4^{-2}.

$$K_2SO_4, Al_2(SO_4)_3, 24H_2O \rightleftharpoons 2K^+ + 2Al^{+3} + 4SO_4^{-2}$$

Thus, in solution double salts contain the ions of the simple salts from which they are derived.

Examples of double salts are Mohr's salt, $FeSO_4 . (NH_4)_2SO_4 , 6H_2O$ and carnallite $KCl, MgCl_2, 6H_2O$, etc.

Complex salts. When ammonia, NH_3, is added to a precipitate of silver chloride, AgCl, the precipitate is dissolved. In this process, ammonia forms a complex ion, $[Ag(NH_3)_2]^+$, which is called the silver-ammonia complex ion. The Ag^+ and the $[Ag(NH_3)_2]^+$ ion are distinct entities. Complex ions are, therefore, the ions which are formed by the combination of an ion with other ions or with neutral molecules. In each of the complex ion, there is a central ion about which the other ions or molecules are grouped in an orderly arrangement. The number of ions or molecules that are arranged around the central ion is called the co-ordination number of the ion. Some examples of complex ions are : $[Cu(NH_3)_4]^{++}$ or $[Cu^{+2}, 4NH_3]$; $[Fe(CN)_6]^{+4}$; $[Co(NH_3)_6]^{+2}$.

A salt which contains a complex ion is called a complex salt. Unlike double salts complex salts are not split up into its component salts in solution. In solution, potassium ferrocyanide ionises to yield complex ions and other ions. Thus,

$$K_4[Fe(CN)_6] \rightleftharpoons 4K^{+1}+[Fe(CN)_6]^{-4}$$
$$[Cu(NH_3)_4]Cl_2 \rightleftharpoons [Cu(NH_3)_4]^{+2}+2Cl^-$$

7.13. Neutralisation. Acids and bases are chemically opposite to each other. When an acid is added to a base, each loses its distinguishing properties. Thus, if an equivalent quantities of an acid and an alkali are mixed, the resulting solution has neither acidic properties nor alkaline properties. On evaporation, the solution gives a solid salt. This reaction is called *neutralisation* (latin, *neuter*, neither). *Neutralisation may be defined as a process by which an acid and a base react to form salt and water.*

For example, if an equivalent quantities of sodium hydroxide and hydrochloric acid are mixed, they undergo the process of neutralisation. The resulting solution is neutral, i.e., neither acidic nor basic. If the solution is evaporated, the salt, NaCl, may be recovered in the solid crystalline form.

$$NaOH+HCl=NaCl+H_2O$$

According to ionic theory, an acid such as HCl when dissolved in water furnishes hydrogen ion and the acidic property of the solution is due to the presence of H^+ ion.

$$HCl \rightleftharpoons H^+ + Cl^-$$

When a base such as NaOH is dissolved in water, it furnishes the hydroxyl ion and the basic property of the solution is due to the presence of OH^- ion.

$$NaOH \rightleftharpoons Na^+ + OH^-$$

So when an equivalent quantities of an acid, HCl, and a base, NaOH, are mixed, the reaction that takes place can be written as

$$H^+ + Cl^- + Na^+ + OH^- = Na^+ + Cl^- + H_2O$$

Since the salt formed dissociates in solution into its ions, Na^+ and Cl^- are present on the both sides of the equation. They truly do not take part in the reaction. The reaction that takes place is *that between the hydrogen ion and the hydroxyl ion to form practically undissociated water molecule* :

$$H^+ + OH^- \rightleftharpoons H_2O$$

Thus, when an acid is added to a base, the sole reaction is the combination of H^+ and OH^- ions which are characteristic of acids and bases respectively. As a result both acidic and basic properties are eliminated ; the solution obtained is neutral since it neither contains H^+ ion nor OH^- ion.

Therefore, *neutralisation can be defined as a process by which water is formed by the reaction of H^+ ion of an acid and the OH^- ion of a base.*

Some neutralisation reactions are explained in the light of ionic theory :

Neutralisation of HCl and H_2SO_4 by $Mg(OH)_2$. In aqueous solution HCl and H_2SO_4 ionise as follows :

$$HCl \rightleftharpoons H^+ + Cl^-$$
$$H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{--}$$

$Mg(OH)_2$ ionises in aqueous solution as follows :

$$Mg(OH)_2 \rightleftharpoons Mg^{++} + 2OH^-$$

Hence, the reaction which takes place when HCl and $Mg(OH)_2$ are mixed in equivalent quantities is

$$2H^+ + 2Cl^- + Mg^{++} + 2OH^- = Mg^{++} + 2Cl^- + 2H_2O$$

Or, $$2H^+ + 2OH^- = 2H_2O$$

In the neutralisation of $Mg(OH)_2$ by H_2SO_4 we get,

$$Mg(OH)_2 + H_2SO_4 = MgSO_4 + 2H_2O$$

Or, $$Mg^{++} + 2OH^- + 2H^+ + SO_4^{--} = Mg^{++} + SO_4^{--} + 2H_2O$$

$$\therefore \quad 2H^+ + 2OH^- = 2H_2O$$

Hence, it is clear from these examples that in all neutralisation reactions, the reaction that takes place is the combination of H^+ ion and OH^- ion to form undissociated water molecule.

7.14. Hydrolysis of salts. Hydrolysis of salt is the reverse process of neutralisation. Salts, as we know, are obtained by the neutralisation of acids by bases. Therefore, we should expect that solutions, at least of normal salts, should react neutral However, all salts other than the salts of strong acids and strong bases do not react neutral when dissolved in water. For instance, if we dissolve some crystals of potassium cyanide KCN in water, the resulting solution reacts alkaline. From this fact, we can only conclude that the potassium cyanide must have reacted with water to form a base. In this reaction, KCN is reversibly split up by water into the free base and the free acid :

$$KCN+HO\ H \rightleftharpoons KOH+HCN$$

Such a reaction between ions of a salt and water is known as hydrolysis (literally means decomposition by water).

Since KOH is a strong base and hydrocyanic acid is a weak acid, the resulting solution reacts alkaline. If the base formed is weak and the acid formed is strong, the resulting solution reacts acidic as in the case of hydrolysis of ferric chloride :

$$FeCl_3+3H.OH \rightleftharpoons Fe(OH)_3+3HCl$$

A salt of strong acid and strong base such as sodium chloride, NaCl, when dissolved in water does not undergo hydrolysis but simply ionises into sodium ion and chloride ion :

$$NaCl \rightleftharpoons Na^++Cl^-$$

These ions have no tendency to combine with either the H^+ or OH^- ions of water, since sodium hydroxide and hydrochloric acid are both strong base and acid respectively.

These experimental facts are explained by ionisation theory. According to this theory, water is slightly ionised in hydrogen ion and the hydroxyl ion :

$$H_2O \rightleftharpoons H^++OH^-$$

When a salt such as potassium cyanide is dissolved into water, it gives positively charged potassium ion and negatively charged cyanide ion :

$$KCN \rightleftharpoons K^++CN^-$$

The negative cyanide ion now reacts with positive H^+, that is,

$$CN^-+H^+ \rightarrow HCN$$

Hydrocyanic acid HCN is a very weak electrolyte and does not undergo appreciable ionisation. Thus, H^+ ions are removed from the solution by binding them up in the form of weak acid HCN. Again, the positive K^+ ion reacts with negative OH^- ion,

$$K^++OH^- \rightleftharpoons KOH$$

Since KOH is a strong base, the K^+ and OH^- ions will remain as ions in solution.

Therefore, the net result is that there is established a hydrolytic equilibrium :

$$KCN+H_2O \rightleftharpoons K^++CN^-+H_2O \rightleftharpoons K^++OH^-+HCN$$

which simplifies to

$$CN^-+H_2O \rightleftharpoons OH^-+HCN$$

Thus, the resulting solution contains excess of hydroxyl ion OH^-

and hence reacts alkaline. It is evident that fundamentally important change that occurs in the hydrolysis of KCN is that the cyanide ions CN^- abstract H^+ ions from water and bind them in the form of unionised HCN, causing new water molecules to ionise, which leads to an accumulation of considerable quantities of hydroxyl ions OH^-, making the solution alkaline.

Hydrolysis is defined as any reaction between the ions of a salt and the ions of water usually accompanied by a change in the concentration of the latter.

The main cause of hydrolysis is the formation of unionised or weakly ionised substances.

We shall now discuss the hydrolysis of three types of salts :

(a) **Hydrolysis of salt of strong acid and weak base.** Salts which are formed by the neutralisation of weak bases such as NH_4OH, $Cu(OH)_2$, $Fe(OH)_3$, etc., (weak bases are formed by the metals other than the alkali metals such as Na, K, Cs, etc.,) and strong acids such as HCl, H_2SO_4, HNO_3, etc., are called the salts of strong acid and weak base. Solutions of these salts are acidic in reaction. For example, when ammonium chloride is dissolved in water, the OH^- ions produced by the dissociation of water unite with NH_4^+ ions to yield undissociated molecules of ammonium hydroxide, thus :

$$H_2O \rightleftharpoons H^+ + OH^-$$
$$NH_4Cl \rightleftharpoons NH_4{}^+ + Cl^-$$
$$NH_4Cl + H_2O \rightleftharpoons NH_4^+ + Cl^- + H^+ + OH^- \rightleftharpoons NH_4OH + H^+ + Cl^-$$

Since HCl is a strong acid, the H^+ and Cl^- will remain as ions in solution. NH_4^+ ions remove OH^- ions from the solution and bind them in the form of unionised NH_4OH. *The solution thus contains excess of H^+ ions and hence reacts acidic.*

The solution of aluminium chloride in water is acidic. This can be explained as follows :

$$AlCl_3 \rightleftharpoons Al^{+3} + 3Cl^-$$
$$3H_2O \rightleftharpoons 3H^+ + 3OH^-$$
$$\overline{AlCl_3 + 3H_2O \rightleftharpoons Al(OH)_3 + 3H^+ + 3Cl^-}$$

$Al(OH)_3$ is a weak base but HCl is a strong acid. Hence, the solution reacts acidic.

Ferric sulphate when dissolved in water undergoes hydrolysis ; the resulting solution is acidic.

$$Fe_2(SO_4)_3 \rightleftharpoons 2Fe^{+3} + 3SO_4^{--}$$
$$6H_2O \rightleftharpoons 6H^+ + 6OH^-$$
$$\overline{Fe_2(SO_4)_3 + 6H_2O \rightleftharpoons 2Fe(OH)_3 + 6H^+ + 3SO_4^{--}}$$

$Fe(OH)_3$ is a weak base but H_2SO_4 is a strong acid. Hence, the aqueous solution of $Fe_2(SO_4)_3$ is acidic.

(b) **Hydrolysis of the salt of weak acid and strong base.** Salts of weak acids such as acetic acid, hydrocyanic acid, carbonic acid, etc., and strong bases such as NaOH, KOH, etc., when dissolved in water react alkaline. For example, water solution of sodium acetate, (CH_3COONa) which is a product of neutralisation of the strong base NaOH and the weak acid CH_3COOH is distinctly basic. Sodium acetate in solution ionises into Na^+ ions and CH_3COO^- ions. The CH_3COO^- ions unite with H^+ ions formed by the dissociation of water to yield undissociated molecules of acetic acid, thus

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$CH_3COONa \rightleftharpoons CH_3COO^- + Na^+$$

$$CH_3COONa + H_2O \rightleftharpoons CH_3COO^- + Na^+ + H^+ + OH^- \rightleftharpoons CH_3COOH + Na^+ + OH^-$$

Since NaOH is a strong base, Na^+ ions and OH^- ions will remain as ions in solution. The CH_3COO^- ions remove H^+ ions from the solution and tie them up in the form of slightly ionised acetic acid. *Thus the solution has excess of OH^- ions and hence is basic in reaction.*

Similarly, the basic character of the aqueous solution of sodium carbonate can be explained :

$$Na_2CO_3 \rightleftharpoons 2Na^+ + CO_3^{--}$$

$$2H_2O \rightleftharpoons 2H^+ + 2OH^-$$

$$\therefore \; Na_2CO_3 + 2H_2O \rightleftharpoons 2Na^+ + 2OH^- + H_2CO_3$$

Sodium hydroxide (NaOH) is a strong base but H_2CO_3 is a weak acid. Hence, the aqueous solution of Na_2CO_3 is alkaline.

(c) **The hydrolysis of salt of weak acid and weak base.** The salts of weak acids and weak bases when dissolved in water may react neutral. The hydrolysis products of these salts are a weak acid and a weak base. For instance, the hydrolysis of ammonium acetate which is a salt of weak acid, CH_3COOH and weak base NH_4OH produces an acid and a base which are approximately equally weak,

$$CH_3COONH_4 \rightleftharpoons CH_3COO^- + NH_4^+$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$CH_3COONH_4 + H_2O \rightleftharpoons CH_3COO^- + NH_4^+ + H^+ + OH^- \rightleftharpoons CH_3COOH + NH_4OH$$

Thus CH_3COO^- ions combine with H^+ ions and bind them in the form of slightly ionised CH_3COOH ; NH_4^+ ions also react with OH^- ions of water and bind them in the form of slightly ionised NH_4OH *Thus the resulting solution, neither contains H^+ ions nor OH^- ions in excess and hence reacts neutral.*

However, if an acid or a base is relatively stronger than the other, then the aqueous solution of the salts will be respectively acidic or alkaline. For example, the aqueous solution of ammonium formate is slightly acidic. Formic acid and ammonium hydroxide are formed by the hydrolysis of ammonium formate :

$$HCOONH_4+H.OH \rightleftharpoons HCOOH+NH_4OH$$

Formic acid and ammonium hydroxide are both weak but formic acid is stronger than ammonium hydroxide. For this reason, the solution is slightly acidic.

If the acid and base produced by the hydrolysis of a salt are either weak or insoluble or volatile, then the hydrolysis of the salt proceeds to completion. For example, when aluminium sulphide is dissolved in water, it is hydrolysed forming aluminium hydroxide $Al(OH)_3$ and H_2S :

$$Al_2S_3+6H_2O \rightleftharpoons 2Al(OH)_3+3H_2S\uparrow$$

H_2S, being a gas, goes out of the solution and $Al(OH)_3$ being insoluble is precipitated. For this reason, Al^{+++} ions and S^{--} ions are removed from the reaction sphere. According to Le Chatelier's principle, the reaction proceeds to completion. Consequently, Al_2S_3 is completely hydrolysed. Similarly, Fe_2S_3 is completely hydrolysed to $Fe(OH)_3$ and H_2S :

$$Fe_2S_3+6H.OH = 2Fe(OH)_3+3H_2S$$

In aqueous solution, ammonium carbonate is hydrolysed evolving carbon dioxide :

$$(NH_4)_2CO_3+2H.OH=2NH_4OH+\underset{\begin{array}{c}\uparrow\downarrow\\ H_2O+CO_2\end{array}}{H_2CO_3}$$

For this reason, the solution reacts alkaline.

The salts of strong acid and strong base do not undergo hydrolysis when dissolved in water. For example, when NaCl which is a salt of strong acid HCl and strong base NaOH is dissolved in water, it ionises into Na^+ ions and Cl^- ions. The Na^+ ions will not combine with OH^- ions of water to form NaOH, since NaOH is completely ionised into Na^+ ions and OH^- ions in solution. Similarly, Cl^- ion will not unite with H^+ ions since HCl is completely ionised. Hence, the concentrations of hydrogen ion and hydroxyl ion will remain the same as in pure water and NaCl solution will be neutral.

Oxide. Oxygen combines with most of the elements to form a class of compounds called oxides. Hence, *oxides are the binary compounds of oxygen with other elements*. The inert gases contained in air do not combine with oxygen and hence do not form oxide. Oxygen can form two covalent bonds by sharing two electrons furnished by another atom. It can also accept two electrons from an atom which donates them and form the oxide ion, O^{--}, i.e.,

$$O+2e \rightarrow O^{--}$$

Non-metallic oxides are mostly covalent compounds whereas many *metallic oxides are ionic compounds.* For example, sulphur dioxide, SO_2, is covalent and cupric oxide, CuO, is ionic.

Classification of oxides. The classification of the oxides is based on their behaviour with water and on the types of the compounds which they form with water. They can be divided into several groups :

(a) **Basic oxides.** *A basic oxide is an oxide which reacts with acids to form salt and water only.* Some basic oxides combine with water to form hydroxides. Generally, basic oxides are produced by the combination of a metal with oxygen. For example, magnesium oxide which is obtained as a result of the reaction between magnesium and oxygen, is a basic oxide because it reacts with acids to form salt and water only, e.g ,

$$MgO+H_2SO_4=MgSO_4+H_2O$$

The oxides of alkali metals such as sodium and potassium and of alkaline earth metals such as calcium and magnesium, readily react with water to form hydroxides which are soluble in water.

$$Na_2O+H_2O=2NaOH \; ; \; CaO+H_2O=Ca(OH)_2$$

On the other hand, majority of the basic oxides do not undergo any reaction with water.

(b) **Acidic oxides.** *The oxides which interact with bases to form salts are called the acidic oxides.*

For example, $CO_2+2NaOH=Na_2CO_3+H_2O$

Acidic oxides are generally the oxides of non-metals and may unite with water to form an acid, e g ,

$$CO_2+H_2O=H_2CO_3 \; ; \; SO_2+H_2O=H_2SO_3$$
$$P_2O_5+3H_2O=2H_3PO_4$$

The oxide of a non-metal from which the acid is derived is called an "acid anhydride", meaning literally an acid without water. Thus, SO_2 is called sulphurous anhydride meaning sulphurous acid without water.

The higher oxides of some metals are also acidic. For example, chromic oxide Cr_2O_3, is basic, while chromium trioxide is acidic :

$$Cr_2O_3+3H_2SO_4=Cr_2(SO_4)_3+3H_2O$$
$$CrO_3+2NaOH=Na_2CrO_4+H_2O$$

Acidic oxides as a rule do not react with acids. There are few exceptional cases where such reactions take place ; these reactions, however, do not lead to the formation of salts. Thus, silicon oxide reacts with hydrofluoric acid to give silicon tetrafluoride which is not a salt :

$$SiO_2+4HF=SiF_4+2H_2O$$

(c) **Amphoteric oxide.** *Oxides which possess the properties of both acidic and basic oxides are known as amphoteric oxides* (the word amphoteric is derived from a greek word meaning both). They interact with bases forming salts, at the same time they dissolve in acids to give salts and water. An example of an amphoteric oxide is aluminium oxide. It interacts with acids to give the salts of these acids.

$$Al_2O_3+3H_2SO_4=Al_2(SO_4)_3+3H_2O$$

whereas its acidic properties are illustrated by its reaction with bases :

$$2NaOH+Al_2O_3=2NaAlO_2+H_2O$$

Zinc oxide, ZnO, stannous oxide, SnO, and plumbous oxide, PbO, are other examples of amphoteric oxide.

(d) **Peroxides**. *The oxides which yield hydrogen peroxide with dilute acids are known as peroxides.* Thus, sodium peroxide and barium peroxide are examples of peroxides, and their reactions with dilute acid can be represented as :

$$Na_2O_2+H_2SO_4=H_2O_2+Na_2SO_4$$
$$BaO_2+H_2SO_4=BaSO_4+H_2O_2$$

(e) **Super-oxides**. Some oxides of alkali and alkaline earth metals contain more oxygen than is necessary for the normal valency of the metals. In these oxides, O_2^{-1} ions are present. An example is potassium super-oxide, KO_2. They react with cold water forming hydrogen peroxide and oxygen.

$$2KO_2+2H_2O=2KOH+H_2O_2+O$$
$$2NaO_2+2H_2O=2NaOH+H_2O_2+O_2$$

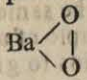
It should be remembered that the peroxide contains O_2^{-2} ion and super-oxide contains O_2^{-1} ion.

(f) **Dioxide or Polyoxide**. Some oxides of certain metals contain more oxygen than their normal oxides, and these oxygen atoms are linked separately to the metal atom by double bonds. For example, lead dioxide and manganese dioxide can be represented as follows :

$O=Pb=O$ (lead dioxide, PbO_2)
$O=Mn=O$ (manganese dioxide, MnO_2)

Such oxides are called dioxides or polyoxides. They do not contain O_2^{-2} or O_2^{-1} group. They react with conc. HCl forming chlorine and conc. H_2SO_4 forming oxygen. But in no case H_2O_2 is formed.

$$PbO_2+4HCl=PbCl_2+2H_2O+Cl_2$$
$$2PbO_2+2H_2SO_4=2PbSO_4+2H_2O+O_2$$

Lead dioxide, PbO_2, and manganese dioxide, MnO_2, are not peroxides because they do not give hydrogen peroxides with dilute acids. Peroxides form a separate group of oxides in which the oxygen atoms are tied not only to the atoms of other elements but between themselves as well. In ordinary oxides, the oxygen atoms are linked chemically to the atoms of other elements only. Thus, sodium peroxide and barium peroxide may be represented by the formulas $Na-O-O-Na$ and  respectively while the formula of lead dioxide is of the type $O=Pb=O$.

(g) **The neutral oxides.** There are certain oxides which neither form hydroxides nor react with bases and acids. Such oxides are called neutral oxides. Nitric oxide, NO, which does not react under any conditions either with acids or with bases is an example of neutral oxide. Carbon monoxide, CO and nitrous oxide, N_2O, are other few examples of such oxides.

(h) **Compound oxides.** These are the oxides which may be regarded as composed of two oxides of the same element. Thus, ferrosoferric oxide, Fe_3O_4, appears to be formed by the combination of ferrous oxide and ferric oxide : $FeO+Fe_2O_3=Fe_3O_4$. This view is supported by its reaction with hot concentrated hydrochloric acid in which a mixture of ferrous and ferric chlorides is formed :

$$Fe_3O_4+8HCl=FeCl_2+2FeCl_3+4H_2O$$

Similarly, red lead Pb_3O_4 is a compound oxide and appears to be composed of lead monoxide PbO (litharge) and lead dioxide PbO_2 since it reacts with hot dilute nitric acid to give a solution of lead nitrate and a precipitate of lead dioxide :

$$Pb_3O_4+4HNO_3=2Pb(NO_3)_2+PbO_2+2H_2O$$

(i) **Suboxides.** This group includes oxides in which the elements are present in combination with a smaller amount of oxygen than is required by their normal valencies. Such oxides are described as suboxides The best known example is carbon suboxide C_3O_2 in which oxygen is present in much smaller amount than is required by the valency of carbon. However, the term carbon suboxide is a misnomer, since this oxide is the anhydride of malonic acid :

$$C_3O_2+2H_2O=CH_2(COOH)_2$$

This oxide should, therefore, be better called an acidic oxide.

EXERCISES

1. What are oxides ? How are they classified ? Give a short account of the different types of oxides.

2. Distinguish between acidic oxide and basic oxide ; normal salt and acid salt ; and double salt and complex salt.

3. Write notes on :

(a) carbon suboxide, (b) amphoteric oxide, (c) hydroxide, (d) bases.

4. Define acid, base, salt, and neutral solution. Explain why solutions of ammonia and of sodium bicarbonate are alkaline and why a solution of sodium bisulphate is acidic (London Inter B. Sc.)

5. Define hydrolysis of salts. Explain why :

(a) Solution of sodium carbonate in water is alkaline.

(b) Solution of ammonium acetate in water is neutral.

(c) Aqueous solution of ferric chloride is acidic.

(d) Aqueous solution of potassium sulphate is neutral.

(e) Aqueous solution of ammonium chloride is acidic.

(f) Aqueous solution of sodium acetate is alkaline.

6. What will happen when

(a) a blue litmus paper is dipped into the solution of each of following salts :

$KClO$, $KClO_2$, $KClO_3$ and $KClO_4$

(b) a red litmus paper is dipped into the solution of each of above salts.

Hints. The acids $HClO$ and $HClO_2$ are weak and $HClO_3$ and $HClO_4$ are strong. Hence, aqueous solutions of $KClO$ and $KClO_2$ are alkaline to litmus paper and those of $KClO_3$ and $KClO_4$ are neutral in reaction.

7. What do you mean by basicity of an acid and acidity of a base ? Explain what is meant by strength of an acid.

8. Which of the following oxides are acid anhydrides and which basic anhydrides ? Write an equation for each representing its reaction with water.

(a) P_2O_5, (b) Na_2O, (c) Cl_2O, (d) CO_2, (e) I_2O_5, (f) Cl_2O_7, (g) N_2O_5 and (h) MgO.

9. Give an account of the different types of salts.

10. Define base. Distinguish between base and alkali.

11. (a) What do you mean by neutralisation ? Explain with examples.

(b) Explain with the help of ionic theory the neutralisation of sodium hydroxide with hydrochloric acid and the neutralisation of calcium hydroxide with sulphuric acid. Give the definition of neutralisation on the basis of this explanation.

12. What do you mean by an acid ? What do you mean by basicity of an acid ? Discuss the ionic theory of acids. What do you mean by strength of an acid or base ?

13. What do you mean by a base. What do you understand by the acidity of a base ? Discuss the ionic theory of bases.

What do you mean by strong acid, and strong base ; weak acid and weak base ? Give examples.

14. What are salts ? Discuss the ionic theory of salts.

15. Write notes on :

(a) normal salts, (b) basic salt, (c) acid salt, (d) complex salt and (e) double salts.

16. What type of oxides are the following ?

Na_2O, SiO_2, Na_2O_2, Fe_2O_3, ZnO, Al_2O_3, CaO, Fe_3O_4, Pb_3O_4, PbO_2, PbO, P_2O_5, SO_2, CuO, K_2O_2, MnO_2, Cl_2O CO_2, MgO, N_2O_5, Cl_2O_7, Cr_2O_3, CrO_3, N_2O, CO, C_3O_4, SnO_2, Mn_3O_4, BaO_2, Ag_2O and Mn_2O_7.

Explain your answer.

17. What is formed by the combination of basic oxide and acidic oxide ? Can the oxide of a non-metal be basic ? Can the oxide of a metal be acidic ?

18. Show that

(i) P_2O_5 is an acidic oxide.

(ii) nitrous oxide and carbon-monoxide are neutral oxide.

(iii) aluminium oxide and zinc oxide are amphoteric oxide.

(iv) carbon dioxide is an acidic oxide.

(v) CrO_3 is an acidic oxide.

(vi) Na_2O_2 is a peroxide.

(vii) PbO_2 is a dioxide.

(viii) calcium oxide is a basic oxide.

19. (i) BaO_2 is a peroxide but PbO_2 or MnO_2 is a dioxide—why ?

(ii) How will you test whether a solution is acidic, basic or neutral ?

20. Explain the following :

(i) The aqueous solution of ammonia and of sodium carbonate are basic but the solution of sodium bisulphate is acidic.

(ii) The aqueous solution of ferric chloride is acidic.

(iii) The aqueous solution of calcium bisulphate is acidic.

(iv) The aqueous solution of ammonium sulphate is acidic.

(v) The aqueous solution of copper sulphate is acidic.

21. Which of the following salts give acidic solution, which basic solution and which neutral solution ? Explain your answer.

$AlCl_3$, $FeCl_3$, $SnCl_4$, $CuCl_2$, Na_2CO_3, NH_4NO_3, Na_3PO_4, NaH_2PO_4, $KAl(SO_4)_2$, $Zn(ClO_4)_2$, $CuSO_4$, $Ba(CN)_2$, $Al(CH_3COO)_3$ and $(NH_4)_2CO_3$.

22. Explain the following statement :

(i) All alkalis are bases but all bases are not alkalis.

(ii) All acids contain hydrogen but all hydrogen-containing compounds are not acids.

(iii) Sodium bisulphate is an acid salt.

(iv) Normal salts are always formed from HCl.

(v) Anhydrous hydrogen chloride cannot turn blue litmus red.

(vi) ClOH acts as an acid but NaOH acts as a base.

(vii) H_3PO_2 is a monobasic acid.

(viii) When Na_2CO_3 is added to the aqueous solution of ferric chloride $Fe(OH)_3$ is precipitated.

(ix) When magnesium is added to the aqueous solution of aluminium chloride bubbles of gases are evolved.

(x) The aqueous solution of ferric chloride on standing becomes turbid.

(xi) The aqueous solution of aluminium sulphate turns blue litmus red.

23. Classify the following compounds into acid salts, basic salts and normal salts :

$NaHCO_3$; Na_2CO_3 ; NH_4Cl ; $KClO_4$; $CuSO_4 \cdot 5H_2O$; NaClO ; Pb(OH)Cl ; $CaCO_3$, $Cu(OH)_2$. [I. I. T., '69]

24. Indicate whether the following statements are true or false. Justify your answer.

(i) Al_2S_3 is completely hydrolysed but $AlCl_3$ is incompletely hydrolysed.

(ii) When Na_2CO_3 is mixed with aqueous solution of $FeCl_3$, CO_2 is not evolved and $Fe(OH)_3$ is not precipitated.

(iii) The aqueous solution of NaH_2PO_4 is slightly acidic and that of Na_3PO_4 is basic.

(iv) When aqueous solution of Na_2S is mixed with the aqueous solution of $CrCl_3$, $Cr(OH)_3$ is precipitated.

(v) When blue litmus paper is dipped into aqueous solution of NaCl, it turns red.

25. When phenolphthalein is added drop by drop to the saturated cold solution of borax the solution turns red. Then acetic acid is added to the solution drop by drop until the red colour is just discharged. If the solution is then diluted, the red colour appears again—Explain.

[**Hints** : $Na_2B_4O_7+3H_2O \rightleftharpoons 2NaBO_2+2H_3BO_3$

$NaBO_2+2H_2O \rightleftharpoons NaOH+H_3BO_3$

when the solution is diluted NaOH is produced in large quantities. H_3BO_3 cannot change the colour of the indicator.]

26. Explain the reaction of potassium sulphide, K_2S and aluminium sulphate in the light of ionic theory.

27. When phenolphthalein is added to the hot concentrated solution of sodium sulphide, the solution turns red but when the solution is cooled, it becomes colourless—Explain.

CHAPTER VIII

TITRATION

Equivalent weights of acids, bases and salts. *The equivalent weight of an acid is defined as the weight of the acid which contains 1·008 parts by weight of replaceable hydrogen.* For example, 36·465 parts by weight of hydrochloric acid contain 1·008 parts by weight of replaceable hydrogen. Hence, the equivalent weight of hydrochloric acid is 36·465. Similarly, 49 parts by weight of sulphuric acid contain 1·008 parts by weight of replaceable hydrogen. 49 is, therefore, the equivalent weight of sulphuric acid. Equivalent weight of an acid when expressed in gram is called *one gram-equivalent weight* or *one gram-equivalent of the acid*. Thus, one gram-equivalent of sulphuric acid is 49 grams. Since the basicity of an acid is the number of replaceable hydrogen atoms, *the equivalent weight of an acid equals its molecular weight divided by its basicity*, i.e.,

$$\text{equivalent weight of an acid} = \frac{\text{molecular weight of the acid}}{\text{basicity of the acid}}$$

Thus, equivalent weight of sulphuric acid

$$= \frac{\text{molecular weight of } H_2SO_4}{2} = \frac{98}{2} = 49$$

(98 is the molecular weight of H_2SO_4).

equivalent weight of phosphoric acid

$$= \frac{\text{molecular weight of } H_3PO_4}{3} = \frac{98}{3} = 32{\cdot}7$$

$$\text{equivalent weight of nitric acid} = \frac{\text{molecular weight of } HNO_3}{1}$$

$$= \frac{63}{1} = 63.$$

The equivalent weight of a base is defined as the weight of the base which can just completely neutralise one equivalent weight of an acid.

The equivalent weight of the base expressed in gram is known as one gram-equivalent of the base.

In the neutralisation reaction between a base and an acid, the fundamental equation is

$$H^+ + OH^- = H_2O \left\{ \begin{array}{l} \text{e.g., } NaOH + HCl \rightleftharpoons Na^+ + |\overline{OH^- + H^+}| + Cl^- \\ \qquad\qquad\qquad\qquad = NaCl + H_2O \\ Ca(OH)_2 + 2HCl \rightleftharpoons Ca^{++} + |\overline{2OH^- + 2H^+}| + \\ \qquad\qquad\qquad\qquad 2Cl^- = CaCl_2 + 2H_2O \end{array} \right.$$

This means that a base which contains one OH^- ion reacts with one equivalent weight of the acid, a base containing two OH^- ions reacts with two equivalent weight of the acid and so on. Since the acidity of the base is the number of hydroxyl groups OH^- it contains, *the equivalent weight of a base equals its molecular weight divided by its acidity*, i.e.,

$$\text{equivalent weight of a base} = \frac{\text{molecular weight of the base}}{\text{acidity.}}$$

Since number of hydroxyl groups which combines with a metal or a radical (such as NH_4^+) to form a base is equal to the valency of the metal, the equivalent weight of the base equals the molecular weight divided by the valency of the metal in it, i.e.,

$$\text{equivalent weight of a basic hydroxide} = \frac{\text{molecular weight of the basic hydroxide}}{\text{valency of the metal}}$$

In the case of basic oxides, the equivalent weight equals the molecular weight of the basic oxide divided by the valency of the metal and by the number of its atoms in a molecule of the oxide, i.e.,

$$\text{equivalent weight of the basic oxide} = \frac{\text{molecular weight of the oxide}}{\text{number of metal atoms} \times \text{the valency of the metal}}.$$

In table 8·1 are illustrated the calculations of the equivalent weights of some common bases and basic oxides.

Table 8·1

Base	Mol. wt. of the base	Acidity	Total valency of the metal	Equivalent wt. of the base
Sodium hydroxide, $NaOH$	40	1	1	$\frac{40}{1}=40$
Calcium hydroxide, $Ca(OH)_2$	74	2	2	$\frac{74}{2}=37$
Ferric hydroxide, $Fe(OH)_3$	107	3	3	$\frac{107}{3}=35{\cdot}67$
Calcium oxide, CaO	56·08	2	2	$\frac{56{\cdot}08}{2}=28{\cdot}04$
Ferric oxide, Fe_2O_3	160	6	6	$\frac{160}{6}=26{\cdot}67$

The equivalent weight of a salt is defined as the weight of the salt which contains one equivalent weight of the metal. Now, the equivalent weight of the metal is obtained by dividing the atomic weight of the metal by its valency. Hence, the equivalent weight of a salt equals the molecular weight of the salt divided by the valency of the metal and by the number of its atoms in a molecule of the salt, i.e.,

$$\text{equivalent weight of the salt} = \frac{\text{molecular weight}}{\text{number of metal atoms} \times \text{its valency}}$$

For example, the equivalent weight of ferric sulphate, $Fe_2(SO_4)_3$ is calculated as follows :

mol. wt. of $Fe_2(SO_4)_3=400$; valency of Fe=3 and number of atoms of Fe=2. Hence, the equivalent weight of $Fe_2(SO_4)_3=\frac{400}{3\times2}=66{\cdot}7$.

Similarly, the equivalent weight of calcium carbonate, $CaCO_3$, is

$$\frac{\text{mol. wt. of } CaCO_3}{1\times2}=\frac{100}{2}=50 \quad \left\{\begin{array}{l}\text{mol. wt. of } CaCO_3=100\\ \text{valency of calcium}=2\end{array}\right.$$

and the equivalent weight of sodium bicarbonate, $NaHCO_3$, is

$$\frac{\text{mol. wt. of } NaHCO_3}{1\times1}=\frac{84}{1}=84$$

The equivalent weight of an acidic oxide is the weight of the oxide which reacts completely with one equivalent of the base. Thus, in the case of CO_2

$$\underset{2\times40}{2NaOH} + \underset{44}{CO_2} = Na_2CO_3 + H_2O$$

we see that two equivalents of sodium hydroxide react with 44 parts by weight of carbon dioxide. Hence, the equivalent weight of carbon dioxide is $44/2=22$.

In the light of ionic theory, we can define the equivalent weight of an acid, base or salt as follows :

An equivalent weight of an acid, base or salt is the fraction of molecular weight that corresponds to one unit of positive or one unit of negative ionic valency. The equivalent weight of an acid, base or salt is, therefore, obtained on dividing the molecular weight by the total positive or negative charges in the formula of the acid, base or salt. Table 8·2 shows how this definition permits one to calculate readily the equivalent weight of a compound.

Standard solutions. To prepare a solution of any substance, it is enough to leave the latter in contact with the solvent for some length of time. Concentration of the solution is defined as the quantity of solute present in a unit volume of solution or in a unit amount of solvent. That is,

$$\text{concentration}=\frac{\text{quantity of solute}}{\text{volume or quantity of solvent or solution}}$$

A solution that contains known amount of solute in a definite volume of solution is called a standard solution. Hence, a standard solution is one of known concentration. There are two methods of expressing concentrations of solutions, viz., (1) weight-volume method and (2) weight-weight method.

(1) **Weight-volume method.** This method consists of stating the weight of a solute in a given volume of solution. Four types of standard solutions depending on this method are discussed below.

Molar solution. *A solution which contains one mole of solute in 1 litre of solution is called molar solution. Molarity is defined*

Table 8·2

(Calculation of equivalent weight of some compounds)

Compound	Ions	Ionic charge	Total valency of the metal/cation	Mol. wt.	Equivalent weight
Hydrochloric acid. HCl	$H^+ + Cl^-$	1	1	36·465	$\frac{36{\cdot}465}{1} = 36{\cdot}465$
Sulphuric acid, H_2SO_4	$2H^+ + SO_4^{-2}$	2	2	98	$\frac{98}{2} = 49$
Oxalic acid, $C_2H_2O_4, 2H_2O$	$2H^+ + C_2O_4^{--}$	2	2	126	$126/2 = 63$
Phosphoric acid. H_3PO_4	$3H^+ + PO_4^{--}$	3	3	98	$98/3 = 32{\cdot}7$
Potassium hydroxide, KOH	$K^+ + OH^-$	1	1	56	$56/1 = 56$
Barium hydroxide, $Ba(OH)_2$	$Ba^{++} + 2OH^-$	2	2	171·36	$\frac{171{\cdot}36}{2} = 85{\cdot}68$
Ferric hydroxide, $Fe(OH)_3$	$Fe^{+++} + 3OH^-$	3	3	107	$107/3 = 35{\cdot}67$
Sodium carbonate, Na_2CO_3	$2Na^+ + CO_3^{--}$	2	2	106	$\frac{106}{2} = 53$
Calcium carbonate, $CaCO_3$	$Ca^{++} + CO_3^{--}$	2	2	100	$\frac{100}{2} = 50$
Ferric chloride, $FeCl_3$, $6H_2O$	$Fe^{+++} + 3Cl^-$	3	3	270·5	$\frac{270{\cdot}5}{3} = 90{\cdot}17$
Aluminium sulphate, $Al_2(SO_4)_3$	$2Al^{+++} + 3SO_4^{--}$	6	6	342·16	$\frac{342{\cdot}16}{6} = 57{\cdot}02$
Copper sulphate, $CuSO_4$, $5H_2O$	$Cu^{++} + SO_4^{--}$	2	2	249·5	$249{\cdot}5/2 = 124{\cdot}75$
Sodium chloride, $NaCl$	$Na^+ + Cl^-$	1	1	58·457	$\frac{58{\cdot}457}{1} = 58{\cdot}457$

as the number of moles of solute contained in one litre of solution. That is

$$\text{molarity}=\frac{\text{number of moles of solute}}{\text{volume of solution in litres}}$$

The number of moles of solute is obtained on dividing the amount of solute in grams by the molecular weight of the solute. A molar solution is denoted by the latter M preceded by a coefficient indicating the "molarity" o' the solution. For example, a 2M solution of sodium chloride contains two moles or $(2\times58{\cdot}458=116{\cdot}92$ grams of sodium chloride (mol. wt. of $NaCl=58{\cdot}458$) in one litre ; a 0·3M solution of it contains 0·3 mole or $0{\cdot}3\times58{\cdot}458=17{\cdot}537$ grams of sodium chloride per litre, etc.

If 53 grams of sodium carbonate are present in 1·5 litres of its solution, then the number of moles of sodium carbonate present in solution is given by

$$\text{number of moles}=\frac{53}{106}\ (\text{molecular weight of } Na_2CO_3=106).$$
$$=0{\cdot}5.$$

Therefore, the molarity of the solution$=\frac{0{\cdot}5}{1{\cdot}5}=0{\cdot}333.$

Equal volumes of solutions of equal molarity contain the same number of moles and hence same number of molecules. So it is very convenient to use molar solutions in volumetric analysis.

Formal solution. In the case of certain compounds, it is found that the formulas do not represent the molecules. This is especially true for ionic compounds such as NaCl which exist as ions even in the solid state. In a solution of NaCl, no NaCl molecules are present but instead only Na^+ and Cl^- ions are present. Hence, in such cases, it is preferable to speak of a formula weight of a substance (formula weight is the sum of the atomic weights of all the atoms in a formula).

A formal or formular solution is one which contains one gram-formula weight (one formula-weight in gram) of solute per litre of solution. The number of gram formula weight (GFW) of solute per litre of solution is called the formality (F). That is,

$$\text{formality (F)}=\frac{\text{number of gram-formula weights}}{\text{litres of solution}}$$

It w grams of solute are dissolved in V litres of solution and a gram is the gram-formula weight of the solute, then the number of gram-formula weight$=\frac{w}{a}$. $\therefore$ formality, $F=\frac{w}{a\times V}$

one formal solution of NaCl is designated as 1 F NaCl, two formal solution of $MgSO_4, 7H_2O$ as 2F $MgSO_4, 7H_2O$ and so on.

If the formula used for a compound is the same as its correct molecular formula describing the molecules actually present in the solution, then the formality and molarity are identical. For example, 2F solution of cane sugar, $C_{12}H_{22}O_{11}$ is also a 2M solution. But a 2F solution of sodium chloride, NaCl, is not a 2M solution. A 2M solution of NaCl is more accurately described as 2M in Na^+ and 2M in Cl^-, since NaCl in solution is completely dissociated into Na^+ and Cl^- ions and no individual NaCl molecules are present in the solution.

Normal solution. *A solution which contains one gram-equivalent of the solute in one litre of solution is called a normal solution.* Normality represents the number of gram-equivalents of solute present in one litre of solution. For example, when 1 gram-equivalent of hydrochloric acid, i.e., 36·465 grams are dissolved in enough water to make one litre of solution, this, by definition, would be one normal solution of hydrochloric acid, i.e., the normality of the solution is 1. If two gram-equivalent weights of this acid, i.e., 72·930 grams are dissolved in enough water to make 1 litre solution, the normality of the solution would become 2. That is,

$$\text{normality (N)}=\frac{\text{number of gram-equivalents of solute}}{\text{volume of solution in litres}}$$

Hence, if the solution contains 0·5 gram-equivalent of the solute per litre, it is called seminormal (0·5N) : if it contains 0·1 gram-equivalent of the solute per litre, it is called decinormal (0·1N) solution, etc. Thus when 1 gram-equivalent weight, i.e., 56·108 grams of KOH are dissolved in enough water to make 1 litre solution, we get 1 N solution of potassium hydroxide, when 0·5 gram-equivalent, i.e., $0{\cdot}5\times56{\cdot}108=28{\cdot}054$ gram are dissolved in enough water to make 1 litre of solution, we get semi-normal (0·5N) solution, when 0·1 gram-equivalent, i.e., $0{\cdot}1\times56{\cdot}108=5{\cdot}6108$ grams are dissolved in enough water to make 1 litre of solution, we get deci-normal (0·1 N) solution of potassium hydroxide, etc.

Since the normality of the solution expresses the number of gram-equivalent weights of solute present, it follows that

$$\text{normality}=\frac{\text{weight of solute in gram present per litre}}{\text{gram-equivalent weight of solute}}$$

Hence, weight of solute in gram per litre

$$=\text{normality}\times\text{gram-equivalent weight.}$$

Thus, the weight of sulphuric acid per litre of a 0·2 N sulphuric acid solution$=0{\cdot}2\times49=9{\cdot}8$ grams, 49 grams being the gram-equivalent of sulphuric acid. On the other hand, if 9·8 grams of sulphuric acid are found to be present per litre of a sulphuric acid solution, then the normality of the solution is $9{\cdot}8/49=0{\cdot}2$.

Volume per cent. A solution which contains one gram of solute in 100 c.c. solution is called one per cent solution. 100 c.c. of a 5% sodium hydroxide solution contain 5 grams of sodium hydroxide. Therefore, we can write

$$\text{Per cent of solute} = \frac{\text{weight of solute}}{\text{volume of solution in c.c.}} \times 100$$

(2) **Weight-weight method.** Chemists commonly use three methods of expressing concentrations of solutions which depend upon giving the weight of both solute and solvent. These methods are (i) Weight per cent (w/w), (ii) molality* and (iii) mole fraction. Since molality and mole fraction are not included in the syllabus they are not discussed here.

Weight per cent. According to this method, a solution which contains one gram of solute in 100 grams of solution is called one per cent solution. A 10 per cent (w/w) solution, therefore, contains 10 grams of solute in 100 grams of solution. Let us suppose that a grams of a solute are dissolved in b grams of a solvent. Hence, the weight of the solution $=(a+b)$ gram.

$\therefore$ $(a+b)$ grams of solution contain a grams of solute.

$\therefore$ 1 gram of solution contain $\frac{a}{(a+b)}$ grams of solute.

$\therefore$ 100 grams of solution contain $\frac{a \times 100}{(a+b)}$ grams of solute.

Hence, percentage strength (w/w) of the solution

$$= \frac{a \times 100}{(a+b)} = \frac{\text{weight of solute in grams}}{\text{total weight of solution in grams}} \times 100$$

Relationship among different units of concentration. One unit of concentration can be converted into the other unit of concentration if sufficient data are available.

(1) **Volume per cent (w/v) and molarity.** Suppose we are given a% (w/v) of a solution and molecular weight of the solute is b.

$\therefore$ 100 c.c. of the solution contain a grams of the solute.

$\therefore$ 1000 c.c. of the solution contain $10a$ grams of the solute.

$\therefore$ Number of moles present in 1 litre of the solution $= \frac{10a}{b}$.

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* A solution which contains one mole of solute in 1000 grams of solvent is known as one molal solution. Molality is defined as the number of moles of solute disolved in 1000 grams of solvent, i.e.,

$$\text{molality} = \frac{\text{number of moles of solute}}{\text{amount of solvent in kilogram}}$$

$\therefore$ Molarity, $M=\frac{a\times 10}{b}$

$\therefore$ $M=\frac{a\times 10}{b}=\frac{a\times 10}{\text{molecular weight of solute}}$

Hence, if the volume per cent (w/v) of the solution and molecular weight of the solute are known, the molarity of the solution can be found out.

Similarly, the relation between volume per cent and formality is found to be $F=\frac{a\times 10}{f}$ where F=formality of a%. (w/v) solution and f=formula-weight of solute.

(2) **Volume per cent (w/v) and normality.** Suppose we are given a% (w/v) of a solution and the equivalent weight of the solute is e. Hence,

100 c.c. of the solution contain a grams of solute.

$\therefore$ 1000 c.c. of the solution contain $a\times 10$ grams of solute.

$\therefore$ Number of gram-equivalents of solute present in 1000 c.c. of the solution$=\frac{a\times 10}{e}$.

$\therefore$ Normality, $N=\frac{a\times 10}{e}$

$$\therefore\quad N=\frac{a\times 10}{e}=\frac{a\times 10}{\text{equivalent weight of solute}}$$

This is the relationship between volume per cent (w/v) and normality of a solution.

(3) **Molarity and Normality.** Let us suppose that we are given N normal solution. Molecular weight of the solute is b and its equivalent weight is e. Then,

1000 c.c. of the solution contain $N\times e$ grams of solute.

$\therefore$ Number of moles present in 1000 c.c. of the solution

$$=\frac{N\times e}{b}.$$

$\therefore$ Molarity of the solution, $M=\frac{N\times e}{b}$

$$\therefore\quad M=\frac{N\times e}{b}$$

$$\therefore\quad \text{molarity}=\text{normality}\times\frac{\text{equivalent weight of solute}}{\text{molecular weight of solute}}\cdot$$

This is the relation between molarity and normality. Similarly, the relation between normality and formality is found to be

$F=\frac{N\times e}{f}$ where F=formality, f=formula-weight of the solute and e is the equivalent weight of solute.

Primary standard solution and secondary standard solution. There are some substances which are readily available in the pure and dry state. These substances can be accurately weighed out with the help of a chemical balance. A standard solution of such a substance can, therefore, be prepared by dissolving a known weight of it in a definite volume of solvent. The standard solution thus obtained is called a *primary standard solution* and the substances whose standard solution can be obtained in this way are called primary standards. Potassium dichromate, oxalic acid, anhydrous sodium carbonate, etc., are examples of primary standards.

On the other hand, there are some substances which cannot be obtained easily in the pure and dry state and it is very difficult to weigh them out accurately. A solution of approximate strength of these substances are first prepared and this solution is then titrated with a suitable primary standard solution to determine its exact strength. A standard solution prepared in this way is called a *secondary standard solution.* Sulphuric acid, sodium thiosulphate, sodium hydroxide, etc., are examples of secondary standards.

Preparation of standard solution. The following example will show clearly how the standard solutions are prepared in the laboratory.

Preparation of 250 c.c. of $\frac{N}{10}$ sodium carbonate solution. The gram-equivalent weight of sodium carbonate is 53 grams. Hence, 5·3 grams of sodium carbonate are required to make 1 litre of $\frac{N}{10}$ sodium carbonate solution. To make 250 c.c. of $\frac{N}{10}$ sodium carbonate solution, $\frac{5\cdot 3}{4}=1\cdot 325$ grams of sodium carbonate are, therefore, required.

Some amount of pure and dry sodium carbonate are taken into a weighing-bottle. The weighing-bottle together with sodium carbonate is then weighed accurately with the help of a chemical balance. Some of sodium carbonate are then poured into a volumetric flask which has a mark on its neck indicating a volume of exactly 250 c.c. and the weighing-bottle is accurately weighed again. Then enough distilled water is added to dissolve all sodium carbonate in the flask after which the flask is filled upto the mark with distilled water. Let us suppose that

the first weight of weighing-bottle = 10·5234 grams

the second weight of weighing-bottle = 9·1728 grams

$\therefore$ the amount of sodium carbonate taken into the flask
$=(10{\cdot}5234-9{\cdot}1728)=1{\cdot}3506$ grams.

Now, 1·325 grams of sodium carbonate in 250 c.c. of solution make $\frac{N}{10}$ solution. Hence, 1·3506 grams of sodium carbonate in 250 c.c. solution make $\frac{1{\cdot}3506}{1{\cdot}325}\left(\frac{N}{10}\right)$, i.e., $1{\cdot}0193\left(\frac{N}{10}\right)$ solution.

Hence, the concentration or strength of the solution is $1{\cdot}0193\left(\frac{N}{10}\right)$. The number 1·0193 is called the factor of $\left(\frac{N}{10}\right)$ sodium carbonate solution.

The factor is obtained on dividing the weight of solute actually dissolved by the theoretical weight required to make a solution of given strength, that is,

$$\text{factor}=\frac{\text{weight of solute actually dissolved.}}{\text{theoretical weight necessary to make a solution of given strength.}}$$

Acidimetry and Alkalimetry. Titration. We have seen that in a neutralisation reaction as in all chemical reactions, the numbers of gram-equivalents of the reacting substances are equal. For example, in the neutralisation of an acid such as HCl with a base such as NaOH, the number of gram-equivalents of the acid must be equal to the number of gram-equivalents of the base. Now, the normality of the solution is related to its volume by the expression ;

$$\text{normality}=\frac{\text{number of gram-equivalents}}{\text{volume in litres.}}$$

$\therefore$ number of gram-equivalents = normality × volume in litres.

Let us now suppose that in a neutralisation reaction V_1 litres of a solution of an acid of concentration C_1 (N) neutralise V_2 litres of a solution of a base of concentration C_2(N). Then

$V_1\ C_1$ = number of gram-equivalents of acid used and
$V_2\ C_2$ = number of gram-equivalents of base used.

It follows, therefore, that for a neutralisation, the product $V_1\ C_1$ for the acid equals the product $V_2\ C_2$ for the base, that is,

$$V_1C_1=V_2C_2 \qquad (8{\cdot}1)$$

Since volume appears on both sides, the volumes V_1 and V_2 need not be in litres. However, V_1 and V_2 must be expressed in the same unit. When the volumes are in millilitres, the product VC represents milliequivalents.

If any three factors of the equation (8·1) are known, the fourth can be calculated. Thus, the relation (8·1) is not only used to calculate the volumes of solutions needed to carry out various reactions, but also used to find the concentrations (normality) of the solutions. *The experimental procedure is known as titration. A titration is an experiment in which we determine the volume of a solution of unknown strength which is needed to react with a definite volume of another solution of known strength.* Since the reactions between acids and bases take place readily and rapidly, the concentrations of solutions of acids and bases may be determined readily by titration. When the unknown concentration of an acid solution is estimated by titration, the process is called *acidimetry* ; while the estimation of unknown concentration of a basic solution is known as *alkalimetry*.

The volumes of solution can be measured accurately by means of burets (fig. 8.1), each with a total capacity of 50 or 100 ml. A buret is a glass tube narrowed at the lower end and fitted with a stop-cock for drawing the solution. The tube is graduated in millilitres and tenth of a millilitre. When a definite volume of a solution has to be measured out at once, a pipet (fig. 8.1) is used.

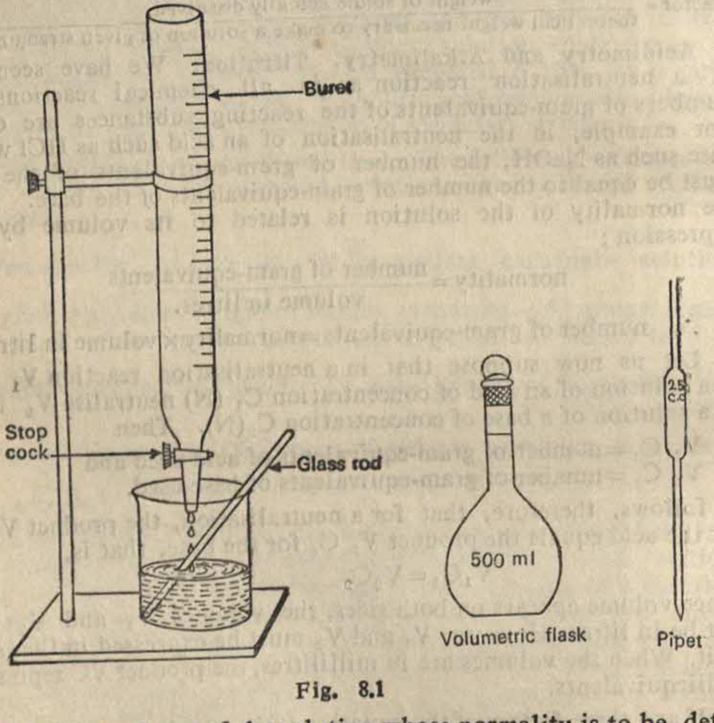


Fig. 8.1

A definite volume of the solution whose normality is to be determined is pipetted out and placed into a beaker. Then a few drops of a solution of an indicator are added to the solution of the beaker. The other solution of known strength is now added from the buret slowly stirring the solution in the beaker constantly, until we reach a point where the indicator shows a permanent change in colour. This is the end point of the titration. The volume of the solution added is read off by the calibrations on the buret. The concentration of the solution which is taken into the beaker is calculated from the relative volumes of the two solutions with the help of the equation (8·1), since that of the other is known.

Indicators used in titration. *An indicator is a substance which changes its colour abruptly as soon as an excess of one substance in the solution is replaced by a very slight excess of the other.* An indicator does not influence the course of a reaction. The indicators used in acid-base titrations are either weak acids, or weak bases. For example, in the neutralisation reactions between acids and alkalis, the indicator may be a solution of phenolphthalein which is colourless in acid solution, but becomes pink immediately after the acid is replaced by a very slight excess of alkali.

The choice of indicators in the titration of acids and bases depends on the strength of acids and bases. In table 8·3 is given a list of indicators which are suitable for a particular type of acid-base titration :

Table 8·3

Indicator	Colour in acid	Colour in alkali	Titration
Any indicator	—	—	strong acid-strong base.
Methyl orange	red	yellow	strong acid-weak base.
Methyl red	red	pale yellow	strong acid-weak base.
Phenolphthalein	colourless	red or pink.	weak acid-strong base.
Litmus	red	blue	strong acid-strong base.

It should be noted that the end point in the titration of an acid with a base is not always in a neutral solution. Only a strong acid titrated with a strong base yields a neutral solution at the end point. A weak acid titrated with a strong base yields a slightly basic solution at the end point. This is due to the fact that when exactly enough number of gram-equivalents of the base has been added to equal the number of gram-equivalents of the acid, the salt (of weak acid and strong base) formed undergoes hydrolysis making the solution slightly alkaline. In such cases phenolphthalein may act as a good indicator. For example, in the titration of acetic acid with sodium hydroxide phenolphthalein acts as a good indicator.

On the other hand, a strong acid titrated with a weak base yields a slightly acidic solution at the end point. This is due to the fact that when exactly enough number of gram-equivalents of the base has been added to equal the number of gram-equivalents of the acid, the salt (of strong acid and weak base) formed undergoes hydrolysis making the solution slightly acidic. In such cases, methyl orange or methyl red may act as a good indicator. For example, in the titration of ammonium hydroxide with sulphuric acid, methyl orange which changes colour in slightly acidic solution would act as a good indicator.

Let us now find how the change in colour of an indicator with the change in acidity or alkalinity of the solution takes place. An indicator may behave as a weak acid of the general formula HIn in which the symbol In stands for a complicated organic substance. An indicator may also behave as a weak base of the general formula InOH.

The indicator behaves as a weak acid and dissociates as :

$$HIn \rightleftharpoons In^- + H^+_a$$

In^- has a different colour from HIn. Thus the red form of litmus may be represented by the formula HIn and the blue form by In^- :

$$\underset{\substack{\text{(red)}\\ \text{(acidic form)}}}{HIn} \rightleftharpoons H^+ + \underset{\substack{\text{(blue)}\\ \text{(basic form)}}}{In^-}$$

In acid solution the concentration of H^+ ions is large and hence the equilibrium is shifted to the left and the indicator assumes the acidic form HIn (red for litmus). In alkaline solution the concentration of OH^- ions is large (and hence H^+ ion is removed from the equilibrium mixture) and hence the equilibrium is shifted to the right. Consequently, in alkaline solution the indicator is converted almost entirely into the basic form, In^- (blue for litmus).

An indicator may be a weak base and dissociates as :

$$\underset{\text{(basic form)}}{InOH} \rightleftharpoons In^+ + \underset{\text{(acidic form)}}{OH^-}$$

In alkaline solution, with concentration of OH^- ions very large the equilibrium is shifted to the left and the indicator assumes the basic form. In acid solution, with concentration of H^+ ions very large, the equilibrium is shifted to the right and the indicator assumes the acidic form.

Example of titration. Preparation of standard solution of sulphuric acid by titration with (N/10) sodium carbonate solution.

The equivalent weight of sulphuric acid is 49. Hence, in order to make 1000 c.c. of $\left(\frac{N}{10}\right)$ H_2SO_4 solution, 4·9 grams of sulphuric acid are to be weighed out. But since sulphuric acid is highly hygroscopic and is not also absolutely pure, it is not weighed. A solution of sulphuric acid of approximately $\left(\frac{N}{10}\right)$ is prepared as follows :

The strength of concentrated sulphuric acid is approximately 36 N. The volume of conc. H_2SO_4 which is to be taken in 1000 c.c. solution to make $\left(\frac{N}{10}\right)$ solution is calculated as follows :

$$36\ \text{N} \times x = \frac{\text{N}}{10} \times 1000$$

$$\therefore \quad x = 2{\cdot}8 \text{ c.c.}$$

Hence, about 2·8 c.c. of conc. H_2SO_4 is measured out by a buret in a 1-litre volumetric flask after which the flask is filled with water upto the mark. This is approximately $\left(\frac{N}{10}\right)$ sulphuric acid solution. This is then titrated with standard sodium carbonate solution.

25 c.c. of standard sodium carbonate solution are taken into a beaker by means of a 25 c.c. pipet. Two or three drops of methyl orange are then added to it, when the colour of the solution becomes yellow. A buret is filled with approximately $\left(\frac{N}{10}\right)$ sulphuric acid solution. Sulphuric acid is then added from the buret drop by drop until the pink colour is just obtained. During titration, the solution in the beaker is constantly stirred. The volume of the acid solution required to neutralise 25 c.c. of sodium carbonate solution is read off by the calibrations on the buret.

Calculation. Let us suppose that the strength of Na_2CO_3 solution $= 1{\cdot}2\left(\frac{N}{10}\right)$

the volume of Na_2CO_3 solution taken = 25 c.c.
the volume of sulphuric acid required = 22·5 c.c.
strength of sulphuric acid = x(N)

Now, from the relation (8·1)

volume of acid × concentration (in normality) of acid
= volume of base × concentration (in normality) of base.

$$22{\cdot}5 \times x = 25 \times 1{\cdot}2\left(\frac{N}{10}\right)$$

$$\therefore \quad x = \frac{25 \times 1{\cdot}2}{22{\cdot}5}\left(\frac{N}{10}\right) = 1{\cdot}3333\left(\frac{N}{10}\right).$$

Therefore, the concentration of sulphuric acid $= 1{\cdot}3333\left(\frac{N}{10}\right)$.

Behaviour of phenolphthalein in the neutralisation of sodium carbonate by acid. The reaction of sodium carbonate with acids takes place in two stages :

$$Na_2CO_3 + HCl = NaHCO_3 + NaCl \qquad (i)$$
$$NaHCO_3 + HCl = NaCl + H_2O + CO_2 \qquad (ii)$$

When two or three drops of phenolphthalein are added to the solution of sodium carbonate, the colour of the solution becomes pink. Sodium carbonate is hydrolysed in aqueous solution and the solution becomes slightly alkaline. In alkaline solution, the colour of phenolphthalein becomes pink.

$$Na_2CO_3 \rightleftarrows 2Na^+ + CO_3^{--}$$
$$2H_2O \leftrightarrows 2H^+ + 2OH^-$$
$$\overline{Na_2CO_3 + 2H_2O = 2Na^+ + 2OH^- + H_2CO_3^{=}}$$

When a strong acid is added to sodium carbonate solution, sodium bicarbonate is first formed and in the resulting solution of sodium bicarbonate phenolphthalein becomes colourless. So when the first stage of the reaction is complete, that is, when only half of Na_2CO_3 is neutralised, phenolphthalein changes its colour from pink to colourless.

This is due to the fact that phenolphthalein is unable to indicate the alkalinity of $NaHCO_3$ solution. Hence, if phenolphthalein is used as an indicator in the titration of sodium carbonate solution with a strong acid, the solution becomes colourless when only half of Na_2CO_3 is neutralised. For this reason, methyl orange is used in the titration of sodium carbonate solution with a strong acid like hydrochloric acid or sulphuric acid.

If 20 c.c. of 1(N) sodium carbonate solution is titrated with 1(N)HCl solution using phenolphthalein as indicator, then after the addition of 10 c.c. of 1(N)HCl, the solution becomes colourless. In order to reach the end point, methyl orange must be added to the half-neutralised solution. If two or three drops of methyl orange are added to this solution, the colour of the solution becomes yellow. After the addition of further 10 c.c. of 1(N)HCl (20 c.c. of 1(N)HCl solution in all), methyl orange changes its colour from yellow to orange and the end point of the titration is indicated.

Relation between volume of a solution and its strength. Let us take V_1 litres of a solution of a substance of normality C_1 and dilute it to a new volume V_2 litres. The concentration of the solution changes and let the new concentration be C_2(N). Since during dilution the number of gram-equivalents of the substance remains the same, we have,

$$V_1C_1 = V_2C_2$$

If the solution is again diluted to a new volume V_3 litres, having the concentration C_3(N), then we get

$$V_1C_1 = V_2C_2 = V_3C_3$$

Thus, when the same solution is diluted to different volumes, V_1, V_2, V_3, V_4, etc., having the concentrations $C_1(N)$, $C_2(N)$, $C_3(N)$, $C_4(N)$, etc., then we get

$$V_1C_1=V_2C_2=V_3C_3=V_4C_4=K \qquad (8\cdot2)$$

where K is a constant which is equal to the number of gram-equivalents present in the solution. From (8·2), it follows :

$$V_1C_1=K \quad \therefore \quad V_1=\frac{K}{C_1}$$

$$\text{i.e.,} \quad V_1 \propto \frac{1}{C_1}\ ; \qquad \text{similarly, } V_2 \propto \frac{1}{C_2}, \text{ etc.}$$

In general, if V is the volume and C is the concentration of the solution, then

$$V \propto \frac{1}{C}$$

Hence, the volume of a given solution is inversely proportional to the concentration of the solution.

Now, let us take V c.c. of a solution of concentration C(N). This solution is diluted to a new volume of concentration 1(N). Denoting the new volume by x, we write by equation (8.2)

$$V \times C(N) = x \times 1(N)$$
$$\therefore \quad x = V \times C \text{ c.c.}$$

Hence, V.c.c. of C(N) solution=(V × C) c.c. of 1(N) solution

For example, 100 c.c. of 1(N) solution contain (49 ÷ 10) = 4·9 grams of sulphuric acid. It is diluted to 1000 c.c. Denoting the new concentration of the solution by x, we write the equation

$$100 \times 1(N) = 1000 \times x$$

$$\therefore \quad x = \frac{N}{10} = 0\cdot1(N).$$

Hence, 1000 c.c. of 0·1(N) H_2SO_4 solution
=1000 × 0·1 c.c of 1(N) H_2SO_4 solution.
=100 c.c. of 1(N) H_2SO_4 solution
=4·9 grams.

Problems

Ex. 1. Calculate the weight of the dissolved substance present in 750 c.c. of 0·2(N) sodium carbonate solution.

Solution. The equivalent weight of sodium carbonate is 53.

Therefore, 1 litre or 1000 c.c. of 1(N) solution of Na_2CO_3 contains 53 grams.

∴ 1000 c.c. of 0·2(N) solution of Na_2CO_3 contain 53 × 0·2 gram

$\therefore$ 750 c.c. of 0·2(N) solution of Na_2CO_3 contain $\frac{53 \times 0{\cdot}2 \times 750}{1000}$
$= 7{\cdot}95$ grams.

Hence, amount of Na_2CO_3 present $= 7{\cdot}95$ grams.

Ex. 2. Find the strength in normality of sodium hydroxide solution which contains 1·5 grams of NaOH in 250 c.c. of the solution.

Solution. 250 c.c. of the solution contain 1·5 grams of NaOH

1000 c.c. of the solution contain $\frac{1{\cdot}5 \times 1000}{250} = 6{\cdot}0$ grams of NaOH.

Now, 40 grams of NaOH in 1000 c.c. make 1(N) solution

$\therefore$ 6 grams of NaOH in 1000 c.c. make $\frac{1 \times 6}{40} = 0{\cdot}15$(N)

$\therefore$ the strength in normality $= 0{\cdot}15$(N).

Ex. 3. In order to neutralise 50 c.c. of sulphuric acid, 20 c.c. of 0·3(N) solution of sodium hydroxide were added. What is the normality of the acid? Calculate the amount of the acid in grams per litre.

Solution. Let the normality of the acid be x
Then, $50 \times x = 20 \times 0{\cdot}3$

$$\therefore \quad x = \frac{20 \times 0{\cdot}3}{50} = 0{\cdot}4 \times 0{\cdot}3 = 0{\cdot}12\text{(N)}$$

Now, the equivalent weight of sulphuric acid is 49.

$\therefore$ 1000 c.c. of 1(N) solution of H_2SO_4 contain 49 grams.
$\therefore$ 1000 c.c. of 0·12(N) solution of H_2SO_4 contain $49 \times {\cdot}12$
$= 5{\cdot}88$ grams.

Hence, normality of the acid $= 0{\cdot}12$(N) and amount of the acid in 1 litre $= 5{\cdot}88$ grams.

Ex. 4. 30 c.c. of a solution of sulphuric acid neutralise 25c .c. of a solution of anhydrous sodium carbonate containing 6·0 grams of the anhydrous substance per litre. Calculate the strength of the acid in terms of normality and grams per litre. [H.S., 1961 (comp.)]

Solution. The equivalent weight of $Na_2CO_3 = 53$.

6 grams of Na_2CO_3 are present in 1 litre of solution. Therefore, the normality of Na_2CO_3 solution $= \frac{6}{53}$(N)

Let the normality of sulphuric acid solution be x. Then

$$x \times 30 = 25 \times \tfrac{6}{53} \quad \therefore \ x = \frac{25 \times 6}{53 \times 30}\text{(N)} = 0{\cdot}0943\text{(N)}$$

$\therefore$ normality of sulphuric acid solution $= 0{\cdot}0943$(N)

The equivalent weight of sulphuric acid is 49. $\therefore$ the amount of sulphuric acid in grams per litre $= 49 \times 0{\cdot}0943 = 4{\cdot}6207$ grams.

Ex. 5. 20·5 c.c. of hydrochloric acid neutralised 25 c.c. of 0·125(N) sodium carbonate solution How will you prepare 1 litre of 0·1(N) hydrochloric acid solution out of it ?

Solution. Let the normality of hydrochloric acid solution be x

Then, $20{\cdot}5\times x=0{\cdot}125(N)\times 25 \quad \therefore\ x=\frac{0{\cdot}125\times 25}{20{\cdot}5}(N)=0{\cdot}1525(N)$.

$\therefore$ strength of hydrochloric acid solution $=0{\cdot}1525(N)$.

Let x c.c. of this solution are to be diluted with water to make 1 litre of 0·1(N) solution.

Then, $x\times 0{\cdot}1525=1000\times 0{\cdot}1 \quad \therefore\ x=\frac{1000\times 0{\cdot}1}{0{\cdot}1525}=655{\cdot}7$ c.c.

It follows, therefore, that to prepare one litre of 0·1(N) solution, 655·7 c.c. of the solution should be diluted with water to make one litre.

Ex. 6. In order to neutralise a solution containing 2·45 grams of an acid, 25 ml of a 2(N) alkali solution were spent. Determine the equivalent weight of the acid. If the acid is dibasic, what will be its molecular weight ?

Solution. 25 ml of 2(N) alkali solution neutralise 25 ml of 2(N) acid solution.

Hence, 25 ml of 2(N) acid solution contain 2·45 grams of the acid.

Hence, 25 ml of 1(N) acid solution contain $=\frac{2{\cdot}45}{2}=1{\cdot}225$ grams of the acid.

$\therefore$ 1000 ml of 1(N) acid solution contain $=\frac{1{\cdot}225\times 1000}{25}$

$=49$ grams.

Hence, the equivalent weight of the acid $=49$ and the molecular weight of the acid $=49\times 2=98$.

Ex. 7. 1·3456 grams of Na_2CO_3 are dissolved in water and the volume of the solution is made upto 250 c.c. 25 c.c. of this solution exactly neutralised 24·85 c.c. of a solution of H_2SO_4. Calculate the normality of (a) Na_2CO_3 solution, (b) acid solution and (c) the amount of Na_2SO_4 formed on neutralisation. [Cal., '52, '53, '63]

Solution. The equivalent weight of $Na_2CO_3=\frac{Na_2CO_3}{2}=\frac{106}{2}=53$.

Now, 250 c.c. of Na_2CO_3 solution contain 1·3456 grams of Na_2CO_3

$\therefore$ 1000 c.c. of Na_2CO_3 solution contain $\frac{1{\cdot}3456\times 1000}{250}$

$=5{\cdot}3824$ grams.

Hence, the normality of Na_2CO_3 solution $=\frac{5{\cdot}3824}{53}=0{\cdot}1016(N)$

∴ 1 litre of 0·0672(N) Na_2CO_3 solution contains 53 × 0·0672 grams of Na_2CO_3.

∴ 250 c.c. of 0·0672(N) Na_2CO_3 solution contain

$$\frac{53 \times 0{\cdot}0672 \times 250}{1000} = 0{\cdot}8904 \text{ grams of } Na_2CO_3.$$

Therefore, 1 gram of impure Na_2CO_3 contains 0·8904 gram of pure sodium carbonate. ∴ 100 grams of impure Na_2CO_3 contains 89·04 grams of pure sodium carbonate.

∴ percentage of pure Na_2CO_3 in the impure sample = 89·04.

Ex. 11. 0·968 gram of NH_4Cl was boiled with 50 c.c. of (N/2) NaOH solution till free from ammonia. 28 c.c. of (N/4)HCl solution were required for neutralising the excess of alkali in mixture. Find the percentage of NH_3 in NH_4Cl.

Solution. 50 c.c. of N/2 NaOH solution ≡ 50 × 0·5 = 25 c.c. of 1(N) NaOH solution.

28 c.c. of N/4 HCl solution ≡ $28 \times \frac{1}{4}$ = 7·0 c.c. of 1(N) HCl solution.

Again, 7·0 c.c. of 1(N) HCl ≡ 7·0 c.c. of 1(N) NaOH

Hence, (25 − 7) = 18 c.c. of 1(N) NaOH solution reacted with NH_4Cl.

Now, 18 c.c. of 1(N) NaOH ≡ 18 c.c. of 1(N) ammonia

Now, 1000 c.c. of 1(N) ammonia contain 17 grams of ammonia.

∴ 18 c.c. of 1(N) ammonia contain $\frac{17 \times 18}{1000} = 0{\cdot}306$ gram of ammonia.

Now, 0·968 gram of NH_4Cl contain 0·306 gram of ammonia

∴ 100 gram of NH_4Cl contain $\frac{0{\cdot}306 \times 100}{0{\cdot}968} = 31{\cdot}6$ gram of ammonia.

∴ percentage of NH_3 in NH_4Cl = 31·6.

Ex. 12. 448 c.c. of hydrogen chloride (gaseous hydrochloric acid) measured at N.T.P. were passed through a solution of sodium hydroxide. When the reaction was over, the solution was found to be still alkaline. In order to neutralise the solution completely 50 c.c. of 2(N) H_2SO_4 solution were added. Calculate the total quantity of NaOH in the solution.

Solution. The gram-molecular weight of hydrogen chloride is 36·5 grams.

Now, 22 4 litres or 22400 c.c. of hydrogen chloride at N.T.P. weigh 36 5 grams.

Now, 1000 c.c. of 1(N) HCl solution contain 36·5 grams.

Hence, 22400 c.c. of hydrogen chloride at N.T.P. ≡ 1000 c.c. of 1(N) HCl solution.

∴ 448 c.c. of hydrogen chloride at N.T.P. $\equiv \frac{1000 \times 448}{22400} = 20$ c.c. of 1(N) HCl solution.

Now, 20 c.c. of 1(N) HCl solution ≡ 20 c.c. of 1(N) NaOH solution.

Again, 50 c.c. of 2(N) H_2SO_4 solution ≡ 100 c.c. of 1(N) H_2SO_4 solution ≡ 100 c.c. of 1(N) NaOH solution.

Hence, amount in c.c. of NaOH solution neutralised $= (20 + 100) =$ 120 c.c. of 1(N) NaOH solution.

Now, 1000 c.c. of 1(N) NaOH solution contain 40 grams of NaOH

∴ 120 c.c. of 1(N) NaOH solution contain $\frac{40 \times 120}{1000} = 4{\cdot}8$ grams of NaOH.

Hence, the total quantity of NaOH in the solution = 4·8 grams.

Ex. 13. To 25 c.c. of $\frac{N}{10}$ H_2SO_4 solution are added 25 c.c. of $\frac{N}{2}$ HCl solution. Calculate the normality of the acid mixture. If the mixture is exactly neutralised by NaOH solution, what will be the weight of salt formed.

Solution. Volume of the acid mixture = 50 c.c.

Now, 25 c.c. of $\frac{N}{10}$ H_2SO_4 solution ≡ 2·5 c.c. of 1(N) H_2SO_4

25 c.c. of $\frac{N}{2}$ HCl solution = 12·5 c.c. of 1(N) HCl solution.

∴ $(2{\cdot}5 + 12{\cdot}5) = 15$ c.c. of 1(N) solution of the mixture are formed.

Let x be the normality of the mixture. Then

$$x \times 50 = 15 \times 1(\text{N})$$
$$\therefore\ x = \tfrac{15}{50} = 0{\cdot}3(\text{N})$$

Hence, strength of the mixture = 0·3(N).

Now, the strength of H_2SO_4 in the mixture $= \frac{25 \times {\cdot}1(\text{N})}{50} = 0{\cdot}05(\text{N})$

the strength of HCl in the mixture $= \frac{25 \times {\cdot}5}{50} = 0{\cdot}25(\text{N})$

Again,

$$\begin{array}{ccccccc} 2NaOH & + & H_2SO_4 & = & Na_2SO_4 & + & 2H_2O \\ 2 \times 40 & & 2 \times 49 & & 2 \times 71 & & \\ \text{2g. eq. wt.} & & \text{2g. eq. wt.} & & \text{2g. eq. wt.} & & \end{array}$$

∴ 50 c.c. of 0·05(N) $H_2SO_4 \equiv$ 50 c.c. of 0·05 (N) Na_2SO_4 solution. Now, 1000 c.c. of 1(N) Na_2SO_4 solution contain 71 grams of Na_2SO_4

∴ 50 c.c. of 0·05(N) Na_2SO_4 solution contain $\frac{71 \times 50 \times 0{\cdot}05}{1000}$ grams of Na_2SO_4 = 0·1775 grams of Na_2SO_4.

Now, 50 c.c. of 0·25(N) HCl ≡ 50 c.c. of 0·25(N) NaCl solution.

∴ 1000 c.c. of 1(N) sodium chloride solution contain 58·5 grams of NaCl.

∴ 50 c.c. of 0·25(N) sodium chloride solution contain

$$\frac{58{\cdot}5 \times 50 \times 0{\cdot}25}{1000} = 0{\cdot}7313 \text{ grams of NaCl.}$$

∴ Amount of salts formed are (a) 0·1775 grams of Na_2SO_4 and (b) 0·7313 gram of NaCl.

Ex. 14. 0·24 gram of a metal was dissolved in 115 c.c. of $\frac{N}{5}$ HCl. The excess of the acid required 30 c.c. of $\left(\frac{N}{10}\right)$NaOH solution for neutralisation.. Calculate the equivalent weight of the metal.

Solution. 30 c.c. of $\left(\frac{N}{10}\right)$ NaOH solution ≡ 30 c.c. of $\left(\frac{N}{10}\right)$ HCl solution.

Now, 30 c.c. of $\left(\frac{N}{10}\right)$ HCl solution ≡ 15 c.c. of $\frac{N}{5}$ HCl solution.

Hence, (115 − 15) = 100 c.c. of $\frac{N}{5}$ HCl reacted with 0·24 gram of the metal.

∴ 1000 c.c of 1(N) HCl solution reacted with 0·24 × 10 × 5 = 12·00 grams of the metal.

∴ Equivalent weight of the metal is 12.

Ex. 15. 25·6 c.c. of $\frac{N}{10}$ $AgNO_3$ solution were required for the titration of 25 c.c. of KCl solution. Find the amount of KCl per litre of the solution. [K=39·1]

Solution. Let the normality of KCl solution be x. Then

$$25 \times x = 25{\cdot}6 \times \frac{N}{10}$$

$$\therefore \quad x = \frac{25{\cdot}6}{25}(N/10) = 1{\cdot}024\left(\frac{N}{10}\right)$$

The equivalent weight of KCl = 74·6

∴ 1000 c.c. of 1(N) KCl solution contain 74·6 grams of KCl

∴ 1000 c.c. of 0·1024(N) KCl solution contain $74·6 \times 0·1024 = 7·64$ grams of KCl.

Hence, the amount of KCl per litre = 7·64 grams.

Ex. 16. 25 c.c. of a solution containing sodium hydroxide and carbonate required 35 c.c. of $\left(\frac{N}{10}\right)$ HCl solution for neutralisation, using phenolphthalein as indicator, when the solution becomes colourless at the end point. To this colourless solution, methyl orange is now added and a further 10 c.c. of $\left(\frac{N}{10}\right)$ HCl solution are required for neutrality. Calculate the amount of NaOH and Na_2CO_3 per litre of the solution.

Solution. Sodium hydroxide and sodium carbonate behave as alkalis towards phenolphthalein but are neutral towards methyl orange. Sodium bicarbonate on the other hand behave as alkalis towards methyl orange but is neutral towards phenolphthalein.

Hence, in the first titration, all the NaOH and half of sodium carbonate are neutralised.

$$Na_2CO_3 + HCl = NaHCO_3 + NaCl$$

∴ 35 c.c. of $\frac{N}{10}$ HCl ≡ all the NaOH + half the amount of Na_2CO_3 present in 25 c.c. of the mixture.

In the second titration, sodium bicarbonate formed which is equal to half of sodium carbonate present in the mixture are neutralised by 10 c.c. of $\frac{N}{10}$ HCl.

$$NaHCO_3 + HCl = NaCl + H_2O + CO_2$$

Hence, 10 c.c. of $\frac{N}{10}$ HCl ≡ half the Na_2CO_3 present in 25 c.c. of the solution.

∴ Amount of Na_2CO_3 present in 25 c.c. of the solution of the mixture ≡ 20 c.c. of $\frac{N}{10}$ HCl solution.

≡ 2 c.c. of 1(N) HCl.

≡ 2 c.c. of 1(N) Na_2CO_3 solution = 0·106 gram of Na_2CO_3

∴ Amount of Na_2CO_3 per litre $= \frac{0·106 \times 1000}{25} = 4·24$ grams.

Again, 35 c.c. of $\frac{N}{10}$ HCl ≡ all the NaOH + 10 c.c. of $\frac{N}{10}$ HCl.

∴ All the NaOH present in 25 c.c. of the mixture

$$\equiv 35 - 10 = 25 \text{ c.c. of } \frac{N}{10} \text{ HCl solution.}$$

∴ 50 c.c. of 0·05(N) $H_2SO_4 \equiv$ 50 c.c. of 0·05 (N) Na_2SO_4 solution. Now, 1000 c.c. of 1(N) Na_2SO_4 solution contain 71 grams of Na_2SO_4

∴ 50 c.c. of 0·05(N) Na_2SO_4 solution contain $\frac{71 \times 50 \times 0{\cdot}05}{1000}$ grams of $Na_2SO_4 = 0{\cdot}1775$ grams of Na_2SO_4.

Now, 50 c.c. of 0·25(N) $HCl \equiv$ 50 c.c. of 0·25(N) NaCl solution.

∴ 1000 c.c. of 1(N) sodium chloride solution contain 58·5 grams of NaCl.

∴ 50 c.c. of 0·25(N) sodium chloride solution contain

$$\frac{58{\cdot}5 \times 50 \times 0{\cdot}25}{1000} = 0{\cdot}7313 \text{ grams of NaCl.}$$

∴ Amount of salts formed are (a) 0·1775 grams of Na_2SO_4 and (b) 0·7313 gram of NaCl.

Ex. 14. 0·24 gram of a metal was dissolved in 115 c.c. of $\frac{N}{5}$ HCl. The excess of the acid required 30 c.c. of $\left(\frac{N}{10}\right)$NaOH solution for neutralisation. Calculate the equivalent weight of the metal.

Solution. 30 c.c. of $\left(\frac{N}{10}\right)$ NaOH solution ≡ 30 c.c. of $\left(\frac{N}{10}\right)$ HCl solution.

Now, 30 c.c. of $\left(\frac{N}{10}\right)$ HCl solution ≡ 15 c.c. of $\frac{N}{5}$ HCl solution.

Hence, $(115 - 15) = 100$ c.c. of $\frac{N}{5}$ HCl reacted with 0·24 gram of the metal.

∴ 1000 c.c of 1(N) HCl solution reacted with $0{\cdot}24 \times 10 \times 5 =$ 12·00 grams of the metal.

∴ Equivalent weight of the metal is 12.

Ex. 15. 25·6 c.c. of $\frac{N}{10}$ $AgNO_3$ solution were required for the titration of 25 c.c. of KCl solution. Find the amount of KCl per litre of the solution. [K=39·1]

Solution. Let the normality of KCl solution be x. Then

$$25 \times x = 25{\cdot}6 \times \frac{N}{10}$$

$$\therefore \quad x = \frac{25{\cdot}6}{25}(N/10) = 1{\cdot}024\left(\frac{N}{10}\right)$$

The equivalent weight of KCl = 74·6

∴ 1000 c.c. of 1(N) KCl solution contain 74·6 grams of KCl

∴ 1000 c.c. of 0·1024(N) KCl solution contain $74{\cdot}6 \times 0{\cdot}1024 = 7{\cdot}64$ grams of KCl.

Hence, the amount of KCl per litre = 7·64 grams.

Ex. 16. 25 c.c. of a solution containing sodium hydroxide and carbonate required 35 c.c. of $\left(\frac{N}{10}\right)$ HCl solution for neutralisation, using phenolphthalein as indicator, when the solution becomes colourless at the end point. To this colourless solution, methyl orange is now added and a further 10 c.c. of $\left(\frac{N}{10}\right)$ HCl solution are required for neutrality. Calculate the amount of NaOH and Na_2CO_3 per litre of the solution.

Solution. Sodium hydroxide and sodium carbonate behave as alkalis towards phenolphthalein but are neutral towards methyl orange. Sodium bicarbonate on the other hand behave as alkalis towards methyl orange but is neutral towards phenolphthalein.

Hence, in the first titration, all the NaOH and half of sodium carbonate are neutralised.

$$Na_2CO_3 + HCl = NaHCO_3 + NaCl$$

∴ 35 c.c. of $\frac{N}{10}$ HCl ≡ all the NaOH + half the amount of Na_2CO_3 present in 25 c.c. of the mixture.

In the second titration, sodium bicarbonate formed which is equal to half of sodium carbonate present in the mixture are neutralised by 10 c.c. of $\frac{N}{10}$ HCl.

$$NaHCO_3 + HCl = NaCl + H_2O + CO_2$$

Hence, 10 c.c. of $\frac{N}{10}$ HCl ≡ half the Na_2CO_3 present in 25 c.c. of the solution.

∴ Amount of Na_2CO_3 present in 25 c.c. of the solution of the mixture ≡ 20 c.c. of $\frac{N}{10}$ HCl solution.

≡ 2 c.c. of 1(N) HCl.

≡ 2 c.c. of 1(N) Na_2CO_3 solution = 0·106 gram of Na_2CO_3

∴ Amount of Na_2CO_3 per litre $= \frac{0{\cdot}106 \times 1000}{25} = 4{\cdot}24$ grams.

Again, 35 c.c. of $\frac{N}{10}$ HCl ≡ all the NaOH + 10 c.c. of $\frac{N}{10}$ HCl.

∴ All the NaOH present in 25 c.c. of the mixture

≡ 35 − 10 = 25 c.c. of $\frac{N}{10}$ HCl solution.

$\equiv$25 c.c. of $\frac{N}{10}$ NaOH solution.

$\equiv$2·5 c.c. of 1(N) NaOH solution.

$\equiv$0·1 gram of NaOH

$\therefore$ Amount of NaOH per litre=4·00 grams.

Ex. 16. 25 c.c. of solution of sulphuric acid neutralise 22·5 c.c. of a 4 per cent solution of sodium carbonate. How would you reduce the strength of the acid to decinormal. [Cal., '48]

Solution. 1000 c.c. of 4 per cent solution of Na_2CO_3 contain 40 grams of Na_2CO_3.

$\therefore$ Normality of 4% Na_2CO_3 solution$=\frac{40}{53}$ (N)=0·7547 (N).

Let the normality of H_2SO_4 be x ; then

$$x \times 25 = 22{\cdot}5 \times 0{\cdot}7547 \text{ (N)}.$$

$$\therefore \quad x = \frac{22{\cdot}5 \times 0{\cdot}7547}{25} = 0{\cdot}6792\text{(N)}.$$

Let 1 litre of this solution be diluted to x litres of normality $\frac{N}{10}$; Then

$$1 \times 0{\cdot}6792 = x \times 0{\cdot}1$$

$$\therefore \quad x = \frac{0{\cdot}6792}{0{\cdot}1} = 6{\cdot}792 \text{ litres.}$$

Hence, 1 litre of the solution should be diluted to 6·792 litres.

Ex. 17. An excess of ferrous sulphide is added to 125 c.c. of dilute sulphuric acid and the volume of hydrogen sulphide set free measured 560 c.c. at 0°C and 760 mm. Calculate the normality of the acid. [Cal., '49]

Solution. $\underset{}{FeS} + \underset{2\times 49}{H_2SO_4} = FeSO_4 + \underset{22{\cdot}4 \text{ litres at N.T.P.}}{H_2S}$

Hence, 22·4 litres of H_2S at N.T.P.$\equiv 2\times 49$ grams of H_2SO_4

$\therefore$ 560 c.c. of H_2S at N.T.P. (at 0°C & 760 mm.)

$$= \frac{2 \times 49 \times 560}{22400} = 2{\cdot}45 \text{ grams of } H_2SO_4$$

$\therefore$ 125 c.c. of dilute H_2SO_4 contain 2·45 grams of H_2SO_4

$\therefore$ 1000 c.c. of dilute H_2SO_4 contain 19·6 grams of H_2SO_4

$\therefore$ Normality of the acid$=\frac{19{\cdot}6}{49}=0{\cdot}4$.

Ex. 18. *Calculate the molarity of a concentrated solution of sulphuric acid which is labelled to be 98% sulphuric acid by weight and whose specific gravity is 1·84.* [I. I. T., '74]

Solution. 100 grams of sulphuric acid contain 98 grams, i.e., 1 mole of sulphuric acid.

$\therefore$ $\frac{100}{1\cdot84}$ c.c. of sulphuric acid solution contain 1 mole of sulphuric acid.

$\therefore$ 1000 c.c. of sulphuric acid solution contain $\frac{1\cdot84 \times 1000}{100} = 18\cdot4$ moles of sulphuric acid

$\therefore$ Molarity of the acid $= 18\cdot4$.

Ex. 19. *The lime obtained on heating 1 gram of calcium carbonate is dissolved in water to make 1 litre of solution. What is the normality of the solution?* [H. S., '81]

$$\underset{100}{CaCO_3} = \underset{56}{CaO} + CO_2$$

100 grams of $CaCO_3$ produce 56 grams of CaO

$\therefore$ 1 gram of $CaCO_3$ produce 0·56 gram of CaO

The equivalent weight of $CaO = \frac{40+16}{2} = 28$

Now, 1 litre of the solution contain 0·56 gram of CaO

$\therefore$ Normality of the solution $= \frac{0\cdot56}{28} = 0\cdot02$

Ex. 20. *10 c.c. of conc. H_2SO_4 (sp. gravity 1·83) is dissolved in water to make 1 litre of solution. 28 c.c. of 0·25(N) Na_2CO_3 solution is required to neutralise 20 c.c. of this solution. Calculate the percentage by weight of acid present in concentrated sulphuric acid.* [H. S., '74]

Let us suppose that strength of dil. $H_2SO_4 = x$(N)

$\therefore$ $20 \times x(N) = 28 \times 0\cdot25(N)$

$$\therefore\ x = \frac{28 \times 0\cdot25}{20} = 0\cdot35$$

Therefore, the strength of dil. $H_2SO_4 = 0\cdot35$(N)

$\therefore$ 1 litre of dilute sulphuric acid contain $0\cdot35 \times 49 = 17\cdot15$ gram of sulphuric acid.

$\therefore$ 10 c.c. of concentrated sulphuric acid contain 17·15 gram of H_2SO_4.

$\therefore$ $10 \times 1\cdot83$ grams of concentrated sulphuric acid contain 17·15 gram of H_2SO_4.

∴ 100 grams of concentrated sulphuric acid contain

$$\frac{17{\cdot}15\times100}{10\times1{\cdot}83}=93{\cdot}71 \text{ gram of } H_2SO_4.$$

Hence, the strength of concentrated sulphuric acid is 93·7 per cent by weight.

Ex. 21. *10 c.c. of $\frac{N}{5}$ H_2SO_4, 6 c.c. of $\frac{N}{2}$ HCl and 20 c.c. of $\frac{N}{4}$ HNO_3 are mixed together. What is the strength of mixture in normality ?*

$$10 \text{ c.c. of } \frac{N}{5}\ H_2SO_4 \equiv 2 \text{ c.c. of } 1(N)\ H_2SO_4$$

$$6 \text{ c.c. of } \frac{N}{2}\ HCl \equiv 3 \text{ c.c. of } 1(N)\ HCl$$

$$20 \text{ c.c. of } \frac{N}{4}\ HNO_3 \equiv 5 \text{ c.c. of } 1(N)\ HNO_3$$

Hence, 10 c.c. of $\frac{N}{5}$ H_2SO_4 + 6 c.c. of $\frac{N}{2}$ HCl + 20 c.c. of $\frac{N}{4}$ $HNO_3 = (2+3+5)$ or 10 c.c. of 1(N) acid mixture.

After mixing, the volume of the acid solution $= 10+6+20=36$ c.c. If its strength is x(N), then

$$x(N)\times36=10\times1(N) \quad \therefore \quad x=\frac{10}{36}=0{\cdot}278.$$

∴ Strength of the mixture = 0·278(N).

Ex. 22. *1·22 grams of a monobasic organic acid gives on complete combustion 3·08 gram of carbon dioxide and 0·54 gram of water. 10 c.c. of $\frac{N}{10}$ barium hydroxide solution is required to neutralize 0·122 gram of the acid. Determine the molecular formula and structural formula of the acid.*

44 grams of carbon dioxide contain 12 grams of carbon

∴ 3·08 gram of carbon dioxide contain $\frac{12\times3{\cdot}08}{44}$ grams = 0·84 gram of carbon.

∴ 1·22 gram of the acid contain 0·84 gram of carbon.

∴ 100 gram of the acid contain $\frac{0{\cdot}84\times100}{1{\cdot}22}=68{\cdot}85$ gram of carbon.

∴ Amount of carbon in the acid = 68·85%

18 grams of water contain 2 grams of hydrogen

∴ 0·54 gram of water contain $\frac{2\times0\cdot54}{18}=0\cdot06$ gram of hydrogen.

∴ 1·22 gram of the acid contain 0·06 gram of hydrogen.

∴ 100 gram of the acid contain $\frac{0\cdot06\times100}{1\cdot22}=4\cdot918$ gram of hydrogen.

∴ Amount of hydrogen in the acid$=4\cdot918\%$

∴ Percentage of oxygen in the acid

$$=100-(68\cdot85+4\cdot918)=26\cdot232$$

$$\therefore\ C:H:O=\frac{68\cdot85}{12}:\frac{4\cdot918}{1}:\frac{26\cdot232}{16}$$
$$=5\cdot74\ :\ 4\cdot918\ :\ 1\cdot64$$
$$=7\ :\ 6\ :\ 2\qquad[\text{ Dividing by }0\cdot82\ ]$$

∴ Empirical formula of the organic acid$=C_7H_6O_2$

∴ Molecular formula of the acid$=(C_7H_6O_2)x$

Now, 10 c.c. of $\frac{N}{10}$ $Ba(OH)_2$ solution≡0·122 gram acid

∴ 1000 c.c. of 1(N) $Ba(OH)_2$ solution≡122 gram of acid

∴ Equivalent weight of the acid$=122$

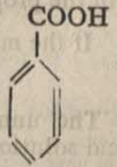
∴ Molecular weight of the acid$=122\times1=122$

∴ $(7\times12+6\times1+2\times16)x=122$

$$\therefore\ x=1$$

∴ Molecular formula of the acid is $C_7H_6O_2$. Since the acid is monobasic, it contains only one carboxylic group (—COOH).

Hence, its structural formula is C_6H_5COOH or



Ex. 23. *A commercial sulphuric acid contains 98% by weight of pure sulphuric acid. Its density is 1·82 gram/c.c. What volume of the acid will be required to prepare 500 c.c. of 0·5(N)* H_2SO_4*-solution ?*

100 grams of commercial sulphuric acid contain 98 grams of H_2SO_4.

∴ $\frac{100}{1\cdot82}$ c.c. of commercial sulphuric acid contain 98 grams or 2 gram-equivalent of H_2SO_4.

∴ 1000 c.c. of commercial sulphuric acid contain

$$\frac{2\times1{\cdot}82\times1000}{100}=36{\cdot}4 \text{ gram-equivalent of } H_2SO_4.$$

∴ Strength of commercial sulphuric acid $=36{\cdot}4$(N)

Let x c.c. of the acid be required to prepare 500 c.c. of 0·5(N) H_2SO_4-solution.

$$\therefore\ x\times36{\cdot}4=500\times0{\cdot}5$$

$$\therefore\ x=\frac{500\times0{\cdot}5}{36{\cdot}4}=6{\cdot}868 \text{ c.c.}$$

∴ The required volume $=6{\cdot}868$ c.c.

Ex. 24. In what proportion by volume an acid of strength 0·7(N) and an alkali of strength 0·3(N) are to be mixed in order to get a (i) neutral solution, (ii) 0·04(N) acidic solution and (iii) 0·04(N) alkaline solution ?

Let us suppose that x c.c. of 0·7(N) acid solution and y c.c. of 0·3(N) alkaline solution are mixed together. The volume of the mixture is $(x+y)$ c.c.

x c.c. of 0·7(N) acid solution $\equiv x\times0{\cdot}7$ c.c. of 1(N) acid solution.

y c.c. of 0·3(N) alkaline solution $\equiv y\times0{\cdot}3$ c.c. of 1(N) alkaline solution.

(i) If the mixture is neutral, then

$$x\times0{\cdot}7=y\times0{\cdot}3$$

$$\therefore\ \frac{x}{y}=\frac{3}{7}.$$

Hence, the acid solution and the alkaline solution are to be mixed in the proportion (by volume) of 3 : 7.

(ii) If the mixture is 0·04(N) acidic, then

$$x\times0{\cdot}7>y\times0{\cdot}3$$

∴ The unneutralised acid solution $\equiv(x\times0{\cdot}7-y\times0{\cdot}3)$ c.c. of 1(N) acid solution.

After mixing the solution, $(x+y)$ c.c. of 0·04(N) acidic solution is produced.

$$\therefore\ (x\times0{\cdot}7-y\times0{\cdot}3)\times1=(x+y)\times0{\cdot}04$$

$$\therefore\ \frac{x}{y}=\frac{17}{33}.$$

Hence, the solution of the acid and the solution of the alkali are to be mixed in the proportion (by volume) of 17 : 33.

(iii) If the mixture is 0·04(N) alkaline, then

$$y\times0{\cdot}3>x\times0{\cdot}7$$

$\therefore$ Unneutralized alkali solution

$$=(y\times 0{\cdot}3-x\times 0{\cdot}7)\text{ c.c. of }1(N)\text{ alkali solution.}$$

After mixing the two solutions, $(x+y)$ c.c. of 0·04(N) alkaline solution is produced.

$$\therefore\ (x+y)\times 0{\cdot}04=(y\times 0{\cdot}3-x\times 0{\cdot}7)\times 1$$

$$\therefore\ \frac{x}{y}=\frac{13}{37}.$$

Hence, the acid solution and the alkali solution are to be mixed in the proportion (by volume) of 13 : 37.

EXERCISES

1. Define equivalent weight and gram-equivalent weight (a) of an acid, (b) of a base and (c) of a salt.

2. Define (a) concentration (b) normal solution and normality (c) molar solution and molarity and (d) formal solution and formality.

How would you prepare a normal and a decinormal solution of sulphuric acid ?

3. Describe the procedure known as titration. You are supplied a bottle of sulphuric acid of approximately 0·1(N) in strength. How will you determine its exact strength ?

4. Show that the product CV represents gram-equivalent weight when V is measured in litres, and milli-equivalent weights when V is measured in millilitres.

5. You are given a mixture of caustic soda and sodium carbonate. Describe how you will determine the percentage composition of the mixture.

6. Explain the following :

(a) 10 c.c. of 1(N) sodium carbonate solution requires 5 c.c. of 1(N) HCl for neutralisation if phenolphthalein is used as indicator. [H.S., '78]

(b) Phenolphthalein is used as an indicator in the titration of weak acid with strong base.

(c) The end point in the titration of an acid with a base is not always in a neutral solution.

(d) Aqueous solution of HCl turns blue litmus red but dry hydrogen chloride gas does not turn blue litmus red.

(e) When a strong base and a weak acid are mixed in chemically equivalent quantities, the resulting solution is not neutral but is basic.

(f) In all chemical reactions, the numbers of gram-equivalent of the reactants and products are equal.

(g) When a strong base and a strong acid are mixed in chemically equivalent quantities, the resulting solution is neutral.

(h) In the titration of the aqueous solution of Na_2CO_3, with aqueous solution of H_2SO_4, methyl orange is used as an indicator instead of phenolphthalein.

7. Arrange the following aqueous solution in the order of decreasing acidity :

1F HNO_2, 1F HCl, 1F NH_4OH, 1F CH_3COONa, 1F CH_3COONH_4, 1F NH_4Cl. 1F CH_3COOH

8. Indicate whether the following statements are true or false. Explain your answer :

(a) 1(M) H_2SO_4 solution is stronger than 1(N) H_2SO_4 solution.

(b) 20 c.c. of 2(M) H_2SO_4 solution just neutralise 20 c.c. of 2(M) NaOH solution.

(c) A 2F solution of sodium chloride, NaCl, is a 2M solution.

(d) Equal volumes of solutions of equal normality contain the same number of moles.

(e) 5 grams of NaOH neutralise more acids than 5 grams of Na_2CO_3.

(f) 5 c.c. of 2M H_3PO_4 solution and 5 c.c. of 2M H_2SO_4 solution contain the same number of molecules.

(g) Any acid contains hydrogen, but any compound containing hydrogen is not an acid.

9. Calculate the equivalent weight of the compound underlined in each of the following equation :

(a) $Ca(OH)_2+\underline{H_3PO_4}=CaHPO_4+2H_2O$ [Ans. 49]

(b) $3NaOH+\underline{H_3PO_4}=Na_3PO_4+3H_2O$ [Ans. 32·66]

(c) $2NaOH+\underline{CO_2}=Na_2CO_3+H_2O$ [Ans. 22]

(d) $CaCO_3+CO_2+H_2O=\underline{Ca(HCO_3)_2}$ [Ans. 81]

Problems

1. Calculate the weight of solute in each of the following standard solutions :

(a) 100 c.c. of $\frac{N}{10}$ H_2SO_4 (b) 25 c.c. of 1(N) KOH. (c) 100 c.c. of $\frac{N}{100}$ HNO_3 and (d) 25 c.c. of $\frac{N}{25}$ NaOH.

[Ans. (a) 0·49 gram. (b) 1·4 grams. (c) 0·063 gram. (d) 0·04 gram.]

2. 20 c.c. of $\frac{N}{10}$ solution of HNO_3 is neutralised by 22·5 c.c. of sodium carbonate solution. Calculate the strength of sodium carbonate in (a) normality, (b) in grams per litre of the solution. [C. U., '16]

[Ans. (a) 0·089 (N) ; (b) 4·717 grams]

3. What volume of 10% solution of sodium carbonate will be required to neutralise a litre of a solution containing 4·9 grams of sulphuric acid. [C.U., '12]

[Ans. 53 c.c.]

4. 20 c.c. of a solution of H_2SO_4 neutralise 21·2 c.c. of a 3 per cent solution of Na_2CO_3. How would you reduce the strength of the acid to decinormal ?

[Ans. 100 c.c. of water to be added to 20 c.c. of the acid] [C. U., '28]

5. A specimen of limestone contains 60% $CaCO_3$. Calculate the amount of stone which will be required to generate just sufficient CO_2 to convert one litre of 1(N) NaOH solution into sodium carbonate. [Ans. 83·3 grams.] [C. U., '31]

6. A solution of caustic soda which contains 4·4 grams per litre is prepared. Calculate the volume of HCl-gas at N.T.P. which when dissolved in water will neutralise 100 c.c. of the alkali solution. [Ans. 0·2464 litre]

[Hints. Normality of NaOH $=\frac{4 \cdot 4}{40}=0 \cdot 11$ (N)

$100\times0\cdot11$(N) NaOH = 11 c.c. of 1(N) NaOH

Now, $NaOH+HCl=NaCl+H_2O$

40 grams of $NaOH \equiv 36{\cdot}5$ grams of HCl gas $\equiv 1000$ c.c. of 1(N) solution.

$\therefore$ 1000 c.c. 1(N) $NaOH \equiv 22{\cdot}4$ litres of HCl gas at N.T.P.

Hence, 11 c.c. 1(N) $NaOH \equiv$?]

7. To 50 c.c. of a solution of HCl, 25 c.c. of 0·82(N) NaOH solution were added. The excess of the acid in the solution required 30 c.c. of 0·09(N) Na_2CO_3 solution for neutralisation. Determine the normality of the acid solution and the number of grams of HCl per litre of the solution. [Cl = 35·5]

[C. U. '21 ; C. U. B. Sc. Part-I, '63]

[Hints : 25 c.c. of 0·82(N) $NaOH \equiv (25 \times 0{\cdot}82)$ or 20·5 c.c. of 1(N) NaOH.

30 c.c. of 0·09(N) $Na_2CO_3 \equiv 2{\cdot}7$ c.c. of 1(N) Na_2CO_3 solution.

$\therefore$ volume of the mixture of alkalis = 23·2 c.c. of 1(N) alkalis.

Now, 50 c.c. of HCl solution $\equiv$ 23·2 c.c. of 1(N) alkalis.

$\therefore$ Normality of HCl solution $= \frac{23{\cdot}2}{50}$ or 0·464(N).

$\therefore$ Amount of HCl per litre $= 0{\cdot}464 \times 36{\cdot}5 = 16{\cdot}936$ grams]

8. To 100 c.c. of sulphuric acid solution, 50 c.c. of 0·2(N) NaOH were added, and for complete neutralisation 20 c.c. of 0·1(N) Na_2CO_3 solution were added. Calculate the strength of H_2SO_4 solution in terms of normality and in grams per litre. [Ans. 0·12(N) ; 5·88 grams]

9. A solution of sodium carbonate is prepared by dissolving exactly 5·83 grams in 1 litre of water. 25 ml. of this solution required 25·5 c.c. of dilute sulphuric acid for neutralisation. Calculate the strength of the acid in normality. What volume of water is to be added to 1 litre of the acid to make it exactly decinormal? [Ans. 0·1078, 78 c.c.]

10. 50 c.c. of a solution of sodium carbonate containing 20 grams of Na_2CO_3 were diluted to 250 c.c. 25 c.c. of the diluted solution required 26 c.c. of a solution of sulphuric acid for neutralisation. Calculate the strength of the acid in grams per litre. [Ans. 71·05 grams]

11. What volume of pure ammonia at 27°C and 750 mm. pressure would be obtained from 10 grams of NH_4Cl ? What volume of (N/10) H_2SO_4 would be neutralised by this ammonia ? [Ans. 4·66, 1·87 litres] [Cal. '19]

12. A weighed amount of ammonium chloride was boiled with excess of strong caustic soda solution and the liberated gas was absorbed by 100 c.c. of a solution containing 4·9 grams of sulphuric acid ; part of the acid was thus neutralised and the excess of acid could be neutralised by 50 c.c. of sodium carbonate solution containing 2·65 grams of Na_2CO_3. Calculate the amount of ammonium chloride originally taken. [Ans. 2·675 grams] [C. U., '55]

13. 0·3 gram of impure sodium carbonate is dissolved in water and the solution is made upto 250 c.c. To 50 c.c. of this solution, 20 c.c. of 0·25(N) HCl is added and the mixture requires for neutralisation 25 c.c. of 0·16(N) NaOH solution. Determine the strength of impure sodium carbonate in terms of normality and the percentage of pure sodium carbonate in the impure sample.

[Ans. 0·02 (N) ; 88·33%]

14. 1·524 grams of NH_4Cl were dissolved in water and 50 c.c. of 1(N) KOH solution were added to it. The total solution was boiled till NH_3 ceased to be evolved, and was then neutralised with 30·95 c.c. of 1(N) H_2SO_4. Find the percentage of NH_3 in NH_4Cl. [Ans. 21·25%] [C.U., '31]

15. 1·08 grams of NH_4Cl were boiled with 62 c.c. of $\left(\frac{N}{2}\right)$ NaOH till free from ammonia. The excess of alkali in the mixture was neutralised by 44 c.c. of N/4 HCl. What is the percentage of ammonia in the salt ?

[Ans. 31·48%] [C. U., '35]

16. A specimen of chalk contained calcium sulphate as impurity. One gram of the solid was treated with 230 c.c. of N/10 HCl solution. The excess of acid in the mixture was completely neutralised by 8·0 c.c. of 0·45 (N) NaOH solution. Calculate the percentage of chalk in the sample. [Ans. 97%] [C. U., '43]

17. An aqueous solution of a dibasic acid containing 0·315 gram requires 35·7 c.c. of 0·14(N) caustic soda solution for complete neutralisation. Determine the molecular weight of the acid. [Ans. 126]

18. 2·205 grams of a dibasic acid are dissolved in water and the volume is made upto 250 c.c. 25 c.c. of this solution require 22·5 c.c. of 0·2(N) sodium hydroxide solution for neutralisation. Calculate the molecular weight and equivalent weight of the acid. [Ans. 98, 49]

19. 560 c.c. of gaseous hydrochloric acid measured at N.T.P. were passed through a solution of NaOH. After the reaction, the solution still remained alkaline. In order to neutralise the solution completely, 50 c.c. of 1·5(N) H_2SO_4 were added to it. Calculate the total quantity of alkali in the solution.

[Ans. 4·00 grams]

20. 0·33 gram of a metal was treated with 50 c.c. of $\left(\frac{N}{2}\right)$ sulphuric acid till the metal dissolved completely. The resulting solution required 15 c.c. of 1(N) sodium hydroxide solution for neutralisation. Calculate the equivalent weight of the metal ? [Ans. 33]

21. 1 gram of the carbonate of a metal was dissolved in 30 c.c. of 1(N) HCl solution. The resulting liquid required 50 c.c. of $\frac{N}{5}$ NaOH solution to neutralise it completely. Calculate the equivalent weight of the carbonate. [Ans. 50]

22. An excess of ferrous sulphide is added to 75 c.c. of dilute sulphuric acid and the volume of hydrogen sulphide set free measured 280 c.c. at 0°C and 760 mm. pressure. What is the normality of the acid ? [Ans. 0·333(N)]

23. Calculate the quantity of a sample of sodium carbonate which contains 80% carbonate and 20% bicarbonate, that should be dissolved in water to make 1 litre solution so that it will require an equal volume of 0·5(N) sulphuric acid solution for complete neutralisation. [Ans. 28 6 grams]

24. 1·6 grams of a mixture of sodium carbonate and bicarbonate were dissolved in water and the volume was made upto 250 c.c. 25 c.c. of this solution neutralised 20 c.c. of 0·125(N) H_2SO_4 solution. Calculate the percentage composition of the mixture. [Ans. bicarbonate = 46·57%, carbonate = 53·43%]

25. SO_2 prepared by the action of excess of strong sulphuric acid on 3·15 grams of copper is passed through a litre of $\frac{N}{5}$ sodium carbonate solution. Find the weight of unchanged sodium carbonate. [Ans. 5·3 grams]

26. A sample of dilute sulphuric acid measuring 50 c.c. when treated with 1 gram of $CaCO_3$ evolved 150 c.c. of CO_2 measured at 27°C and 700 mm. pressure. Calculate the strength of the acid in grams per litre and the amount of $CaCO_3$ remaining unchanged. [Ans. 10·9956 grams ; 0·4392 gram]

27. A standard KCl solution is made by dissolving 7·46 grams of the salt in a litre of the solution. 25 c.c. of this solution require 20 c.c. of a solution of $AgNO_3$ to precipitate all the chloride as silver chloride. Calculate the normality of $AgNO_3$ solution and also the amount of AgCl formed.

[Ans. 0·125(N) ; 0·3587 gram]

28. 20 c.c. of a mixture of nitric acid and hydrochloric acid when treated with excess of silver nitrate solution, gave 0·8 gram of silver chloride. 100 c.c. of the same mixture required 40 c.c. of 1(N) NaOH solution for neutralisation.

Calculate the weight of nitric acid and hydrochloric acid present in 1 litre of the mixture. [Ans. HCl ; 10·174 grams ; HNO_3, 8·14 grams]

29. (a) A laboratory bottle is labelled 12N HCl. How would you make from it 20 c.c. of 3N HCl ? [Ans. 5 c.c. of 12(N) solution is to be diluted with water to 20 c.c.] [H. S., '78]

(b) 5·6 litres of dry ammonia gas at S.T.P. is passed through 1 litre of 1(N)H_2SO_4. What volume of 0·1(N) KOH will be required to neutralise the mixture ? [Ans. 7·5 litres] [H. S., '78]

30. (a) What is the molarity and molality of a 13% solution (by weight) of sulphuric acid ? Its density is 1·090 g/ml. To what volume should 100 ml. of this acid be diluted in order to prepare a 1·5(N) solution ?

[Ans. 1·44, 1·53, 192 c.c.] [I. I. T., '78]

(b) Two litres of ammonia at 30°C and at 0·2 atm pressure neutralised 134 ml. of a solution of sulphuric acid. Calculate the normality of the acid.

[Ans. 0·12(N)] [I. I. T., '78]

31. (i) A solution of a mixture of potassium chloride and potassium hydroxide was neutralised with 120 ml. of 0·12(N)HCl. Calculate the amount of KOH in the mixture. (ii) After titration, the resultant solution was made acidic with nitric acid. Then excess of silver nitrate solution was added to precipitate the silver chloride which weighed 3·7 gram after drying. Calculate the percentage of potassium hydroxide in the original mixture.

[Ans. 0·8064 gram ; 48·71%] [I. I. T., '73]

32. Conc. sulphuric acid has a density of 1·84 g/ml. at 25°C and contains 98 per cent of acid by weight. What volume of the concentrated acid should be used to prepare 1000 litres of 0·5 molar sulphuric acid solution at 25°C.

[Ans. 27·17 litres] [I. I. T., '71]

33. Upon heating a litre of a N/2 HCl solution, 2·675 gram of hydrogen chloride is lost and the volume of the solution shrinks to 750 ml. Calculate (i) the normality of the resultant solution, and (ii) the number of milli-equivalents of HCl in 100 ml. of the original solution.

[Ans. 0·569(N), 50] [I. I. T., '75]

34. Calculate the molarity of a concentrated solution of sulphuric acid which is labelled to be 98% sulphuric acid by weight and whose specific gravity is 1·84.

[Ans. 18·4] [I. I. T., '74.

35. 25 c.c. of a 1·05 $\frac{N}{10}$ Na_2CO_3 solution require 20·1 c.c. of a solution of sulphuric acid for neutralisation. What volume of this acid is to be diluted so as to prepare 1 litre of exactly $\frac{N}{10}$ sulphuric acid solution ? What indicator would you use for this titration ? [Ans. 769·2, Methyl orange] [H.S., '72]

36. A 10 ml. portion of $(NH_4)_2SO_4$ solution was treated with an excess of NaOH. The ammonia gas evolved was absorbed in 50 ml. of 0·1N HCl. 10 ml. of 0·2N NaOH was required to neutralise the remaining HCl. How many grams of $(NH_4)_2SO_4$ are in a litre of solution. [Ans. 19·8 grams] [I. I. T., '74]

37. 1 gram of a mixture, consisting of equal number of moles of carbonate of two alkali metals, required 44·4 ml. of 0·5N hydrochloric acid for complete reaction. If the atomic weight of one of the metals is 7, find the atomic weight of the other metal. What will be the total amount of sulphate formed on quantitative conversion of 1 g. of the mixture into sulphates ?

[Ans. 23 ; 1·4 gm.] [I. I. T., '72]

38. A sample of a metal (M) carbonate was neutralised by 10 ml. of 0·1(N) hydrochloric acid and the resulting chloride gave 0·0517 gram of the phosphate $[M_3(PO_4)_2]$. Calculate the equivalent weight of M (the formula of phosphoric

acid is H_3PO_4. What other experimental data would you require to determine the atomic weight of M ? Indicate the method based on this data. [I. I. T., '68]
[Ans. 20·03]

39. 60 c.c. of 0·1N H_2SO_4 solution are mixed with 40 c.c. of 0·2N HCl solution. Calculate the strength of the resulting solution. [Ans. 0·14N]

40. In what proportion by volume, would a solution of 0·04(N)HCl be mixed with a solution of 0·2(N)H_2SO_4 to produce a solution of exactly decinormal ? [Ans. 5 : 3]

41. 1·66 gram of a dibasic organic acid when burnt in air gives 3·52 gram of carbon dioxide and 0·54 gram of water. 100 c.c. of $\frac{N}{10}$ $Ba(OH)_2$ solution is required to neutralise 0·83 gram of the acid. Deteremine the molecular formula and structural formula of the acid.
[Ans. $C_8H_6O_4$, $C_6H_4(COOH)_2$

42. 1 gram of oleum is diluted by mixing with water. The solution requires 44 c.c. of 0·5(N) sodium hydroxide solution for neutralisation. Calculate the percentage of free sulphur trioxide in oleum. [Ans. 34·66%]

[Hints : [$SO_3+2NaOH=Na_2SO_3+H_2O$; $H_2SO_4+2NaOH=Na_2SO_4+2H_2O$]

43. In what proportions 0·4(N) acid and 0·5(N) alkali solution are to be mixed in order to get (i) neutral solution, (ii) 0·1 N) alkaline solution and (iii) 0·1(N) acidic solution ? [Ans. (i) 5 : 4 (ii) 4 : 5 (iii) 2 : 1]

44. 10 c.c. of a solution of HCl exactly neutralise 15 c.c. of a solution of NaOH. Also 10 c.c. of the same HCl solution, when treated with excess of $AgNO_3$ solution give 0·1435 gram of AgCl. Find out the strength of NaOH solution in grams/litre. (Ag=108) [Ans. 2·667 gram/litre] [J. E. E., '75]

45. In what proportion 0·2(N) of an acid is to be mixed with 0·5(N) of another acid to get a resultant solution of 0·3(N) strength ? [Ans. 2 : 1]

CHAPTER IX

GENERAL PROPERTIES OF GASES

Introduction. When a given quantity of a gas is enclosed in a vessel, it spreads uniformly throughout the entire space of the vessel, whatever may be the volume of the vessel. In other words, a gas is infinitely expandable. Again, the gases are also easily compressed. Let us consider a cylinder (fig 9.1) containing a gas. The cylinder is fitted with a movable piston. It is possible to exert pressure on the piston by adding weights. If we exert a very small pressure on the gas by placing a very small weight on the piston, the volume of the gas does not decrease. This proves that the gas itself is exerting an opposing pressure. Now, if we increase the pressure on the gas by placing large weights so that it exceeds the opposing pressure, the volume of the gas will decrease somewhat. The more is the pressure on the gas, the smaller will be the gas volume. Thus, there exists a relationship between the volume occupied by a specified quantity of gas and the external pressure which is exerted upon it.

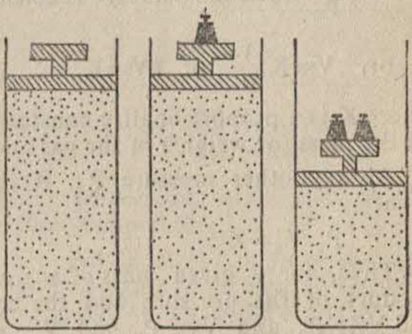


Fig. 9.1

Again, it is a common experience that gases expand when heated and contract when cooled. Thus, three variables are involved in the study of physical behaviour of any given mass of a gas—Pressure (P), temperature (T) and volume (V). The relationship between any two of the three variables may be studied, provided the other variable remains constant.

We shall discuss three possible relationships : (1) Boyle's law relating pressure and volume, temperature being held constant, (2) Charles' law relating temperature and volume, pressure being kept constant, and (3) Gay-Lussac's law relating temperature and pressure, volume being held constant.

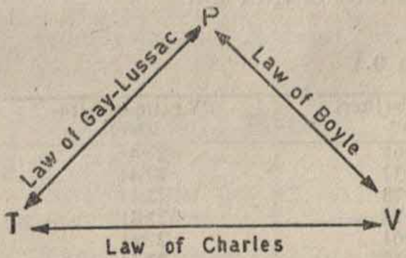


Fig. 9.2

Change in volume of a gas with pressure : Boyle's law. In 1662, Sir Robert Boyle (1617-1691), an English scientist, determined experimentally the relationship between the volume of a given mass of gas and the external pressure which is exerted upon it. He summarised his experimental results in the statement now called Boyle's law. It may be stated as : *At constant temperature, the volume occupied by a given mass of a gas is inversely proportional to the pressure.*

If P is the pressure and V is the volume of a given mass of a gas, then Boyle's law can be expressed mathematically as :

$V \propto \frac{1}{P}$ when temperature is constant.

$$\text{or,}\quad V=K\frac{1}{P} \quad \text{or}\quad PV=K, \tag{9·1}$$

where K is a proportionality constant, the value of which depends on the mass (or weight) of the gas and the temperature.

At any other pressure P_2, if the corresponding volume is V_2, then

$$P_2V_2=K \tag{9·2}$$

Thus, for a given mass of any gas at constant temperature, the product of the pressure and the corresponding volume such as P_1 and V_1 ; P_2 and V_2 ; P_3 and V_3, etc., will be equal to the same constant value, i.e.,

$$P_1V_1=K\ ;\ P_2V_2=K\ ;\ P_3V_3=K, \text{etc.}$$

$$\text{Hence, } P_1V_1=P_2V_2=P_3V_3= \quad \dots \quad \dots=K. \tag{9·3}$$

That is, at constant temperature, the product of the pressure and the corresponding volume of a given mass of a gas is constant.

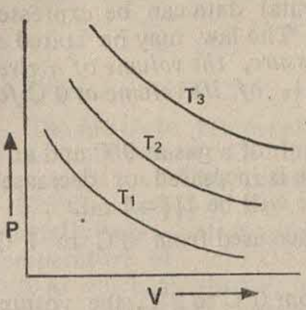
$$\text{Now, } P_1V_1=P_2V_2\ ;\ \frac{P_1}{P_2}=\frac{V_2}{V_1}$$

The volumes obtained by applying different pressures at 0°C on 4 grams of helium are given in table 9.1. It is found that the product PV is constant. This illustrates Boyle's law.

Table 9.1

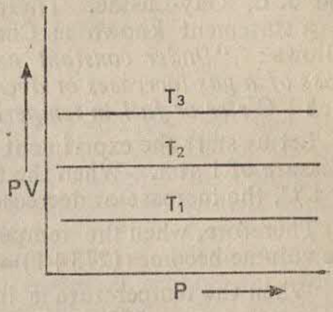
Pressure (atmosphere) 'P'	Volume (liter) 'V'	PV (atmosphere-liter)
1·0852	20·65	22·41
1 0020	22·37	22·41
0·8067	27·78	22·41
0·6847	32·73	22·41
0·5387	41·61	22·41
0·3550	63·10	22 41
0·1937	115·65	22·41

In order to represent graphically the relation between pressure and volume, the volumes are represented along ordinate and the pressures along abscissa. The nature of the curve is shown in fig. 9·3 (a) which represents graphically the Boyle's Law.



$T_3 > T_2 > T_1$

Fig. 9.3(a)



$T_3 > T_2 > T_1$

Fig. 9 3(b)

The curve in fig. 9·3(a) is called "isothermal" since they represent the behaviour of gases at constant temperature.

The relation between pressure and density. Boyle's law can be extended to deduce the relation between pressure and density of a gas. Let a given mass m of a gas at a constant temperature possesses a volume V_1 and density ρ_1 at pressure P_1, and volume V_2 and the density ρ_2 when the pressure is P_2. Since the mass of the gas remains constant, we have

$$\rho_1=\frac{m}{V_1} \quad \text{and} \quad \rho_2=\frac{m}{V_2}$$

Hence, $\rho_1 V_1=\rho_2 V_2=m$ or, $\frac{\rho_1}{\rho_2}=\frac{V_2}{V_1}$ (9·4)

Again, from Boyle's law :

$$P_1 V_1=P_2 V_2 \quad \text{or} \quad \frac{P_1}{P_2}=\frac{V_2}{V_1} \qquad (9\cdot5)$$

From (9·4) and (9·5) we get $\frac{P_1}{P_2}=\frac{\rho_1}{\rho_2}$ or, $\frac{P_1}{\rho_1}=\frac{P_2}{\rho_2}=K$ (constant) (9·6)

$\therefore\ P_1=K\times\rho_1\ ;\ P_2=K\times\rho_2$

Hence, $P \propto \rho$

Therefore, *the density of a given mass of a gas at constant temperature is directly proportional to the pressure.*

Change in volume of a gas with temperature : Charles' law. Let us consider how the volume of a given mass of a gas varies with change in temperature if the pressure is kept constant. It is a common experience that when a gas is heated, its volume increases and when it is cooled, its volume decreases. The numerical relationship between the increase in temperature and the corresponding increase in volume was determined experimentally by J. A. Charles and J. L. Gay-Lussac. Their experimental data can be expressed in a statement known as Charles' law. The law may be stated as follows : "*Under constant external pressure, the volume of a given mass of a gas increases or decreases by* $\frac{1}{273}$ *of its volume at* 0°C *for each* 1°C *rise or fall in temperature.*"

Let us start the experiment with 273 ml. of a gas at 0°C and at a pressure of 1 atm. When the temperature is increased or decreased by 1°C, the increase or decrease of volume will be $\frac{273}{273}=1$ ml.

Therefore, when the temperature is increased from 0°C to 1°C, the volume becomes $(273+1)=274$ ml.

When the temperature is increased from 0°C to 2°C, the volume becomes $\left(273+2\frac{273}{273}\right)=273+2=275$ ml.

When the temperature is increased from 0°C to 10°C, the volume becomes $\left(273+10\frac{273}{273}\right)=273+10=283$ ml.

When the temperature is increased from 0°C to 100°C, the volume becomes $\left(273+100\frac{273}{273}\right)=273+100=373$ ml.

In the similar way,

when the temperature is lowered from 0°C to −1°C, the volume becomes $(273-1)=272$ ml.

When the temperature is lowered from 0°C to −2°C, the volume becomes $\left(273-2\frac{273}{273}\right)=273-2=271$ ml.

When the temperature is lowered from 0°C to −10°C, the volume becomes $\left(273-10\frac{273}{273}\right)=273-10=263$ ml.

When the temperature is lowered from 0°C to −273°C, the volume becomes $\left(273-273\frac{273}{273}\right)=273-273=0$ ml. (9·7)

At constant pressure, the volume of a gas thus depends upon temperature. Let us assume that a given mass of a gas occupies the volume V_0 at 0°C. At any higher temperature t°C, it then occupies the volume V_t. Therefore, we have

$$V_t=V_0+\text{expansion} \qquad (9\cdot8)$$

The expansion for 1°C rise in temperature is $\frac{V_0}{273}$. Hence, for t°c rise in temperature, the expansion is $\frac{V_0}{273}\times t$.

From (9.8) we get

$$V_t = V_0 + \frac{V_0}{273}t = V_0\left(1+\frac{t}{273}\right) = \frac{V_0}{273}(273+t) \qquad (9\cdot9)$$

When $t=-273$°C, $V_t=0$.

The absolute temperature. From (9·7) and (9·9), we find that if the temperature is lowered to −273°C, the volume of the gas becomes 0 c.c. This means that the gas occupies no volume at −273°C. Although this condition could not be realised experimentally because all gases liquefy before −273°C is reached, the temperature of −273°C is a very important one. It is the temperature at which, in theory, the volume occupied by the gas would become zero. This temperature is called the absolute zero and is the foundation of a scale of temperature which is not man-made like the centigrade and fahrenheit temperature scales but rather is based upon a natural behaviour of matter.

The absolute scale of temperature. The relation between the absolute and centigrade scales of temperature. A new scale of temperature may now be defined which has its zero 273 degrees below the zero on the centigrade scale. This new temperature scale is called the absolute temperature scale (symbol °A) or the Kelvin temperature scale (°K) in honour of Lord Kelvin who formulated it. The magnitude of the degree, and hence an interval is identical on both scales. Thus 0°K becomes −273°C and 0°C becomes 273°K. Hence, 100°C becomes 373°K. The relation between Centigrade scale and the Kelvin scale is thus given by $T\,(°K)=t(°C)+273$; or, $t(°C)=T(°K)-273$. (9·10)

Thus, to convert Centigrade to Kelvin, we add 273 to the centigrade temperature ; to convert Kelvin to Centigrade, we subtract 273 from the Kelvin temperature.

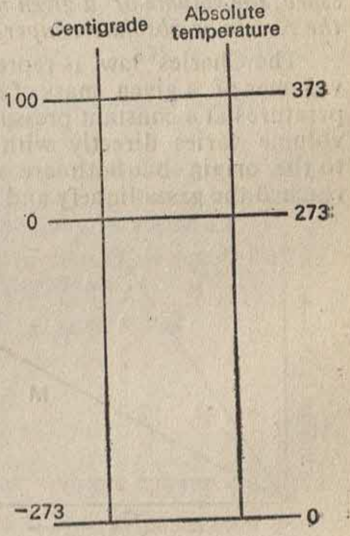


Fig. 9.4

From equation (9·9), we may now write

$$V = \frac{V_0}{273}(273+t) = \frac{V_0}{273}T \qquad (9\cdot11)$$

where V is the volume at t°C

For a change of temperature, t_1, above 0°C, the volume V_1 is given by

$$V_1=\frac{V_0}{273}(273+t_1)=\frac{V_0}{273}T_1 \qquad (9{\cdot}12)$$

where T and T_1 are the absolute temperatures.

Hence,

$$\frac{V}{V_1}=\frac{V_0}{273}T\times\frac{273}{V_0T_1}=\frac{T}{T_1}; \quad \text{or,} \quad \frac{V}{T}=\frac{V_1}{T_1}$$

Similarly, $\frac{V}{T}=\frac{V_1}{T_1}=\frac{V_2}{T_2}=\text{constant}=K$ (say)

$$\text{or,} \quad \frac{V}{T}=K \qquad \therefore \quad V=K\times T \qquad (9{\cdot}13)$$

where the constant K depends upon the quantity of gas and the pressure. Hence, $V \propto T$.

Hence, the Charles' law may be stated thus : *At constant pressure, the volume of a given mass of a gas is directly proportional to the Kelvin or absolute temperature.*

The Charles' law is represented graphically below. In fig. 9·5, volumes of a given mass of a gas is plotted against absolute temperatures at a constant pressure. The straight line indicates that the volume varies directly with temperature. Both the lines 'point' to the origin but both are dotted to indicate that before 0°K is reached the gases liquefy and then solidify.

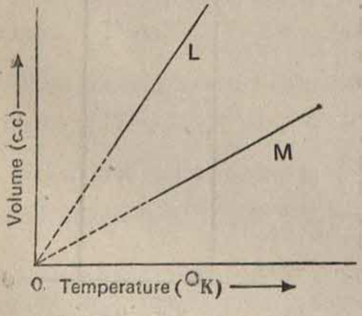


Fig. 9.5 : L → for volume of the gas which is 273 ml. at 273°K. M → for volume of the gas which is 100 ml. at 273°K.

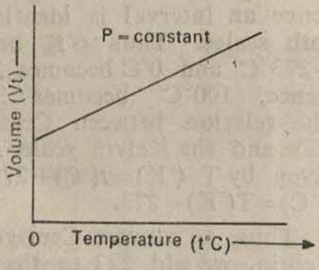


Fig. 9.6

The curves in fig. 9.5 and 9.6 are called "isobars" because they represent behaviour of gases at constant pressure.

When volumes of a given mass of a gas is plotted against temperatures on the centigrade scale at a constant pressure, a curve like that in the fig. 9.6 is obtained.

In fig. 9.7 volumes of a given mass of a gas are plotted against temperatures at different constant pressures. It is seen that all the lines meet the X-axis at $-273°C$ or, $0°K$.

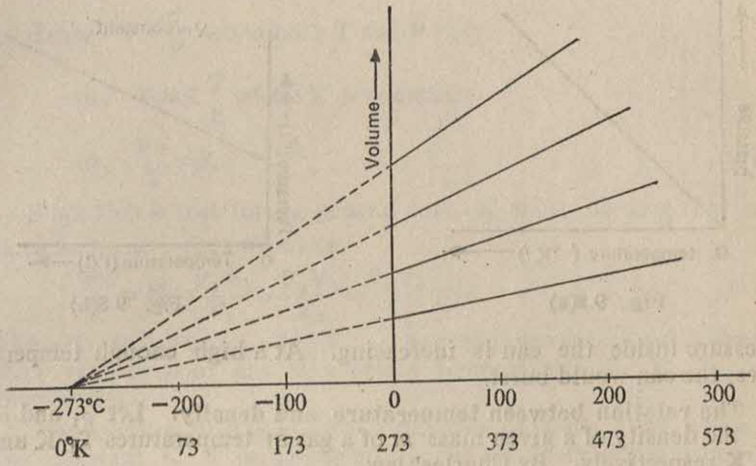


Fig. 9.7 : Change of volumes of gases with temperature at different constant pressures.

Gay-Lussac's law. The numerical relationship between temperature and pressure at constant volume may be given in a statement known as Gay-Lussac's law. The law may be stated as :

At constant volume, the pressure exerted by a given mass of a gas is directly proportional to its absolute temperature.

- Gay-Lussac's law can be expressed mathematically as :

$P \propto T$ when V is constant

$$\text{or, } P=KT \quad \text{or, } \frac{P}{T}=K. \qquad (9{\cdot}14)$$

For the same sample of a gas at constant volume but for different temperatures T_1 and T_2, we have

$$\frac{P_1}{T_1}=\frac{P_2}{T_2}=K \quad \text{or, } \frac{P_1}{P_2}=\frac{T_1}{T_2}$$

The relationship between pressure and temperature at constant volume is illustrated graphically in fig. 9.8(a) and 9.8(b). The curves in fig. 9.8(a) and 9.8(b) are called 'isochore' because they represent the behaviour of gases at constant volume.

An experimental test of the law may be made in the following manner :

An tin can is filled with air and tightly closed. If the can is heated, the walls of the can will bulge out indicating that the pressure inside the can is increasing. At a high enough temperature, the can would burst.

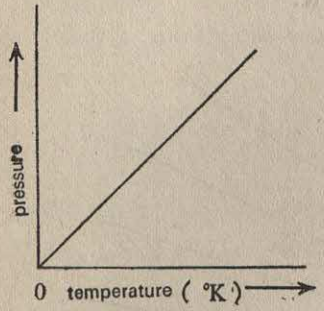


Fig. 9.8(a)

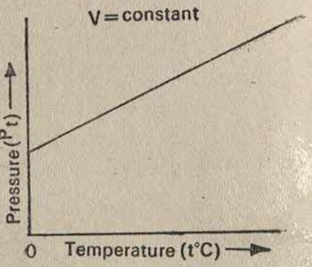


Fig. 9 8(b)

The relation between temperature and density. Let ρ_1 and ρ_2 be the density of a given mass m of a gas at temperatures T_1°K and T_2°K respectively. By Charles' law,

$\frac{V_1}{T_1}=\frac{V_2}{T_2}$ (at constant pressure) where V_1 and V_2 are volumes of the gas at temperatures T_1°K and T_2°K respectively.

$$\text{or, } \frac{V_1}{V_2}=\frac{T_1}{T_2} \qquad (9{\cdot}15)$$

Since the mass of the gas remains constant, we have

$$\rho_1=\frac{m}{V_1} \text{ and } \rho_2=\frac{m}{V_2} \quad \text{or, } \frac{\rho_2}{\rho_1}=\frac{m}{V_2}\times\frac{V_1}{m}=\frac{V_1}{V_2} \qquad (9{\cdot}16)$$

From (9·15) and (9·16), $\frac{\rho_2}{\rho_1}=\frac{T_1}{T_2}$ $\therefore$ $\rho_1 T_1=\rho_2 T_2=K$ (constant)

(9·17)

$$\therefore \ \rho T=K \text{ (constant)} \qquad \text{or, } \rho=\frac{K}{T} \quad \text{or, } \rho \propto \frac{1}{T}$$

Thus, *pressure remaining constant, the density of a given mass of a gas varies inversely as the absolute temperature.*

The combined or ideal gas law. In chemical work, one is often interested in the variation of the volume of a gas with both temperature and pressure. In such a case, both the law of Boyle and Charles can be combined elegantly into a single equation.

Let V be the volume of a given mass of a gas at pressure P and at temperature T°A. Then

(i) By Boyle's law, $V \propto \frac{1}{P}$ when T is constant.

(ii) By Charles' law, $V \propto T$ when P is constant.

Hence, $V \propto \frac{T}{P}$ when both T and P vary.

or, $V = K\frac{T}{P}$ where K is constant.

$$\text{or,} \quad \frac{PV}{T} = K \tag{9·18}$$

Since this is true for the general case, it must be true for any particular case ; thus we write

$$\frac{PV}{T} = K = \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} = \frac{P_3V_3}{T_3} = \ldots \tag{9·19}$$

where P_1, V_1 ; P_2, V_2 ; P_3, V_3 ; ...are the pressures and volumes of the same mass of gas at absolute temperatures $T_1, T_2, T_3, \ldots\ldots$ respectively.

The equation 9·18 is known as equation of state. The value of the constant K is proportional to the quantity of gas. Let the quantity of the gas be one mole (one mole centains $6\ 023 \times 10^{23}$ molecules). According to Avogadro's hypothesis, one mole of all gases under the same conditions of temperature and pressure occupies the same volume. Hence, the value of K is the same for one mole of all gases, independent of the conditions under which measurements are made on the gases. The value of the constant K when one mole of gas is taken, is known as molar gas constant and is denoted by the special symbol R. Hence, for one mole of the gas, the equation (9·18) assumes the form

$$\frac{PV}{T} = R \quad \text{or,} \quad PV = RT$$

where V is the volume of 1 mole of the gas.

Now, V is the volume of 1 mole of a gas at pressure P and temperature T. Then the volume of *n* moles of the gas at the same pressure (P) and temperature (T°K) is given by

$$n \times V = v$$

Hence, for *n* moles of the gas

$$P \times n \times V = nRT$$

$$\therefore \quad P \times v = nRT \tag{9·20}$$

where *v* is the volume of *n* moles of the gas.

The equation (9·20) is known as the ideal or perfect gas law. There are four variables, any one of which can be calculated if the other three are known.

If '*g*' grams of a gas of molecular weight M are taken under consideration, then the number of moles, $n=\frac{g}{M}$. Hence, the equation (9·20) becomes $Pv=\frac{g}{M}RT$. (9·21)

The equation (9·21) may be modified further to correlate density ;

$$P=\frac{g}{v}\times\frac{RT}{M} \text{ or } P=\rho\frac{RT}{M}\left(\text{since } \rho=\frac{\text{mass}}{\text{volume}}=\frac{g}{v}\right) \quad (9\cdot22)$$

Combined effect of temperature and pressure on the density of gases.

Let ρ be the density of a given mass of a gas at temperature T°K and at pressure P. Then

(i) by Boyle's law, $\rho \propto P$ when T is constant.

(ii) by Charles' law, $\rho \propto \frac{1}{T}$ when P is constant.

Hence, $\rho \propto \frac{P}{T}$ when both P and T vary.

or, $\rho=K\frac{P}{T}$ where K is a constant.

$$\text{or, } \frac{\rho T}{P}=K \quad (9\cdot23)$$

If ρ_1, ρ_2, ρ_3,...be the densities of the same mass of a gas at temperatures T_1, T_2, T_3, ...and at pressures P_1, P_2, P_3, ..., then

$$\frac{\rho_1T_1}{P_1}=\frac{\rho_2T_2}{P_2}=\frac{\rho_3T_3}{P_3}= \quad \dots \quad \dots \quad \dots \quad =K$$

$$\text{Hence, } \frac{\rho T}{P}=\frac{\rho_1T_1}{P_1}=\frac{\rho_2T_2}{P_2}=\frac{\rho_3T_3}{P_3} \quad (9\cdot24)$$

Deviations from the gas laws. Ideal and Real gases. The laws of Boyle and Charles are not obeyed exactly by the gases over an extensive range of temperature and pressure. In other words, experimental determination is not in exact agreement with the theoretical calculation. At ordinary temperature and pressure, such deviations from the gas laws are not large but the deviations are larger, the lower is the temperature. At high pressures, the deviations are also very large. The concept of a gas which would obey the gas laws exactly is, however, of great value to scientists. *A gas which obeys gas laws under all conditions of temperature and pressure is called an ideal gas.* Real or actual gases, on the other hand, do not behave strictly in accordance with the gas laws. The following are, therefore, the criteria of the ideality of a gas :

(i) it will obey exactly the idealised gas equation

$$Pv=nRT$$

(ii) the volume of an ideal gas would be zero at 0°K.

No such gas (ideal gas) really exists in nature. Real gases are said to be more or less ideal by the degree to which they approximate to the gas laws. *Under the conditions of high temperatures and low pressures, the real gases generally approach the ideal behaviour.*

The numerical value of the gas costant R. The gas constant R is given by the expression $R=\frac{PV}{T}$ for one mole of an ideal gas, where $P=\text{pressure}=\frac{\text{force}}{\text{area}}$, $V=\text{volume}$, $T=\text{temperature}$.

$$\text{Hence, } R=\frac{\text{force}}{\text{area}}\times\text{volume}\times\frac{1}{\text{temperture}}\text{ per mole.}$$

$$=\text{force}\times\frac{\text{volume}}{\text{area}}\times\frac{1}{\text{temperature}}\text{ per mole.}$$

$$=\text{force}\times\text{length (i.e., distance)}\times\frac{1}{\text{temperature}}\text{ per mole.}$$

$$=\text{work per mole per degree absolute.}$$

Therefore, R can be expressed in absolute units of work. Hence, R will have different values in different systems of units.

It is known that one mole, i.e., a gram-molecule of any gas occupies 22·412 litres at N.T.P. From this fact, the value of R can be found out in different units as follows :

The value of R in C.G.S. units.

Normal pressure=76 cm of mercury.

The density of mercury at 0°C=13·596 grams per c.c. Therefore, the mass of the column of mercury 76 cm in height and 1 sq. cm in area=13·596×76 grams.

Hence, normal pressure in absolute units=13·596×76×980·6 dynes per sq. cm. (where g=gravitation constant=980·6).

$$V=22{\cdot}412\text{ litres}=22{\cdot}412\times1000\text{ c.c.}$$

$$T=0+273=273^\circ\text{A}.$$

Hence, $R=\frac{PV}{T}=\frac{76\times13{\cdot}596\times980{\cdot}6\times22{\cdot}412\times1000}{273}$ ergs per degree per mole.

$$=8{\cdot}315\times10^7\text{ ergs per degree per mole.}$$

$=8{\cdot}315$ joules per degree per mole (since 1 joule$=10^7$ ergs)

The value of R in calories. We have

$$R=8{\cdot}315\times10^7\text{ ergs per degree per mole.}$$

But 1 calorie $=4{\cdot}183\times10^7$ ergs.

Hence, $R=\frac{8{\cdot}315\times10^7}{4{\cdot}183\times10^7}=1{\cdot}985$ calories per degree per mole.

The value of R in litre-atmosphere. The value of R is given by the equation

$R=\frac{PV}{T}$ for one mole of an ideal gas.

If P is expressed in atmosphere and V in litres, then volume of one mole of a gas at N.T.P. $=22{\cdot}412$ litres ; normal presssure $=1$ atmosphere and $T=0+273=273^\circ A$.

$R=\frac{1\times22{\cdot}412}{273}=0{\cdot}0821$ litre-atmosphere per degree per mole.

The students should memorise the values of R in different units. These are given below :

$R=8{\cdot}315\times10^7$ ergs per degree absolute per mole.
$=8{\cdot}315$ joules per degree absolute per mole
$=0{\cdot}0821$ litre-atmosphere per degree absolute per mole.
$=1{\cdot}985$ (nearly 2) calories per degree absolute per mole.

The approximate value $R=2$ calories per degree absolute per mole finds many applications in the discussion of the problems concerning gases.

The normal temperature and pressure. From the general gas law, it is clear that the volume of a given mass of a gas will depend both on the absolute temperature and on the pressure. It is useful to express the amount of a gas in terms of volume, but obviously this would have no meaning unless temperature and pressure were also specified. For this reason, a standard temperature and pressure have been agreed upon as a basis for comparing or stating gas volumes. The standard or normal temperature is 0°C or 273°K and the standard pressure is 1 atmosphere at sea level (or 760 mm. of mercury). These standard conditions are also called normal (or standard) temperature and pressure and are often abbreviated as N.T.P. or (S.T.P.).

Dalton's law of partial pressure. John Dalton (1800) after many measurements upon mixtures of gases which do not react chemically enanciated the law known as the law of partial pressures. It states that *the total pressure of a mixture of gases is equal to the sum of the partial pressures of the gases in the mixture.*

The partial pressure of any component of a mixture of gases is defined as the pressure which the component would exert if it existed alone in the volume occupied by the mixture at the same temperature.

Let us suppose that a quantity of a gas A is enclosed in a 1-litre vessel. Let this gas has a pressure of 0·5 atm at 0°C. Let another gas B enclosed in another 1-litre vessel at the same temperature has a pressure of 0·75 atm. When both the gases are placed in a single 1-litre vessel, the total pressure of the mixture will be (0·5+0·75)=1·25 atm. The partial pressure of the gas A in the mixture is 0·5 atm and that of B in the mixture is 0·75 atm provided the temperature remains constant in all cases.

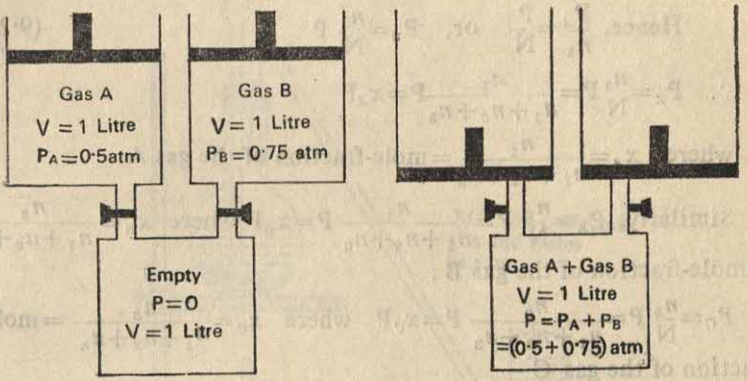


Fig. 9.9

Calculation of partial pressures. The gas laws are applicable not only to individual gases but also to mixtures of gases. Let n_1 moles of A, n_2 moles of B and n_3 moles of C are mixed together and the volume of the mixture be V. The partial pressures of A, B and C are P_A, P_B and P_C respectively. The total pressure of the gas-mixture is given according to Dalton's law.

$$P=P_A+P_B+P_C \tag{9·25}$$

Now, the gas A has its volume V under its partial pressure P_A. Applying gas laws, we get,

$$P_A V=n_1 RT \quad \text{or,} \quad P_A=\frac{n_1 RT}{V} \tag{9·26}$$

Similarly, $P_B=\frac{n_2 RT}{V}$ and $P_C=\frac{n_3 RT}{V}$ since the temperature in all cases remains the same.

Hence, we get,

$$P=P_A+P_B+P_C=n_1\frac{RT}{V}+n_2\frac{RT}{V}+n_3\frac{RT}{V}$$

$$=(n_1+n_2+n_3)\frac{RT}{V}=N\frac{RT}{V} \tag{9·27}$$

where N is the total number of moles present in the mixture.

From (9·26), $\frac{RT}{V}=\frac{P_A}{n_1}$

From (9·27), $\frac{RT}{V}=\frac{P}{N}$

Hence, $\frac{P_A}{n_1}=\frac{P}{N}$ or, $P_A=\frac{n_1}{N}P$ (9·28)

$\therefore\ P_A=\frac{n_1}{N}P=\frac{n_1}{n_1+n_2+n_3}P=x_A P$

where $x_A=\frac{n_1}{n_1+n_2+n_3}$ = mole-fraction of the gas A

Similarly, $P_B=\frac{n_2}{N}P=\frac{n_2}{n_1+n_2+n_3}P=x_B P$ where $x_B=\frac{n_2}{n_1+n_2+n_3}$ = mole-fraction of the gas B ;

$P_C=\frac{n_3}{N}P=\frac{n_3}{n_1+n_2+n_3}P=x_C P$ where $x_C=\frac{n_3}{n_1+n_2+n_3}$ = mole-fraction of the gas C

Hence, the partial pressure of a component gas of a gas-mixture = mole-fraction of the component gas × total pressure of the mixture.

Hence, it is possible to calculate the partial pressures of the components of the gas mixture.

Alternatively, we can derive the expression for partial pressures of gases. Let V_1 c.c. of gas A at pressure P_1, V_2 c.c. of gas B at pressure P_2 and V_3 c.c. of gas C at pressure P_3 be mixed together. Let the total volume of the mixture be $(V_1+V_2+V_3)=V$ c.c. P_A, P_B and P_C are the partial pressures of the gases A, B and C in the mixture respectively. The total pressure of the mixture, according to Dalton's Law, is given by

$$P=P_A+P_B+P_C$$

By Boyle's law, $P_1V_1=P_AV$; $P_2V_2=P_BV$ and $P_3V_3=P_CV$

$$\text{Hence, } P_A=\frac{P_1V_1}{V}=\left(\frac{V_1}{V_1+V_2+V_3}\right)P_1$$

$$P_B=\frac{P_2V_2}{V}=\left(\frac{V_2}{V_1+V_2+V_3}\right)P_2$$

$$P_C=\frac{P_3V_3}{V}=\left(\frac{V_3}{V_1+V_2+V_3}\right)P_3$$

The total pressure $P=P_A+P_B+P_C$

$$=\left(\frac{V_1}{V_1+V_2+V_3}\right)P_1+\left(\frac{V_2}{V_1+V_2+V_3}\right)P_2+\left(\frac{V_3}{V_1+V_2+V_3}\right)P_3$$

$$=\frac{P_1V_1+P_2V_2+P_3V_3}{V_1+V_2+V_3}.$$

Pressure of gases collected over water. Dalton's law is applicable to gases collected over water. In the laboratory, the gases which are not soluble in water are usually collected by the displacement of water. Some water evaporates into the space occupied by the gas and intermingles with it. Hence, we get a mixture of the collected gas and water vapour. The total pressure of the mixture, according to Dalton's law, is equal to the sum of the partial pressure of the collected gas and the partial pressure of water vapour at the temperature of the experiment. The partial pressure of water vapour is also known as *aqueous tension.*

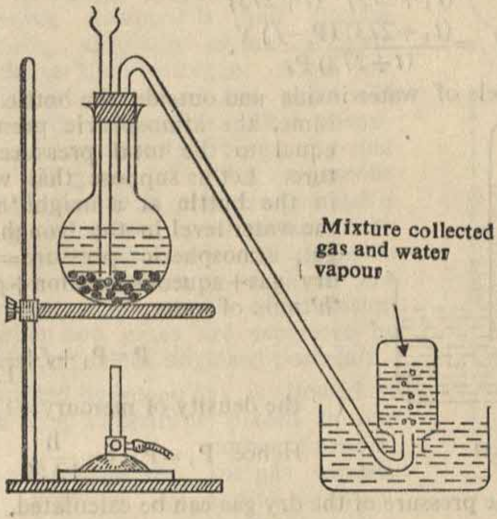


Fig. 9.10

The total pressure of the mixture is equal to the atomspheric pressure if the water level is the same inside and outside the bottle into which the gas is collected. The atmospheric pressure is obtained from the barometric reading. Thus, if P is the total pressure of the mixture, P_1 is the partial pressure of the collected gas and f is the aqueous tension, then

$$P = P_1 + f \quad \text{or,} \quad P_1 = P - f. \qquad (9{\cdot}29)$$

i.e., pressure of the dry gas = atmospheric pressure — aqueous tension at t°C (t°C is the temperature at which the gas is collected).

Let us assume that

(i) the volume of the moist gas at t°C = V c. c.
(ii) the aqueous tension at t°C = f mm. of mercury.
(iii) the barometric pressure = P mm. of mercury.

Hence, the pressure of the dry gas = (P—f) mm. of mercury.

If the gas occupies a volume V_1 c.c. at temperature t_1°C and at pressure P_1 mm. of mercury, then V_1 can be calculated by applying gas laws as follows :

$$\frac{P_1 V_1}{(t_1+273)} = \frac{V(P-f)}{(t+273)}$$

$$\therefore \quad V_1 = \frac{(t_1+273)(P-f)V}{(t+273)P_1}. \qquad (9{\cdot}30)$$

If the levels of water inside and outside the bottle are not the same, the atmospheric pressure is not equal to the total pressure of the mixture. Let us suppose that water stands in the bottle at a height 'h' mm above the water level in the trough. Then we get, atmospheric pressure=pressure of dry gas+aqueous tension+pressure of 'h' mm. of water.

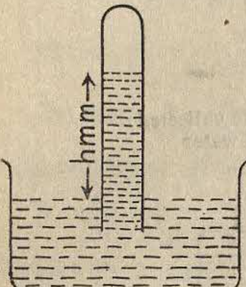


Fig. 9.11

$$P = P_1 + f + \frac{h}{13.59}.$$

($\because$ the density of mercury=13.59 gm./cc)

$$\text{Hence} \quad P_1 = P - f - \frac{h}{13.59}$$

from which the pressure of the dry gas can be calculated.

Diffusion of gases. All gases have the tendency to intermingle with one another. Thus, when a gas-jar is filled with hydrogen and is placed above another gas-jar filled with air mouth to mouth, the particles of hydrogen move downwards and penetrate the air, and air moves upwards and penetrate hydrogen. The movement of the gases will continue until the molecules of the gases are uniformly spread throughout the entire space of the gas-jar. Finally, we get a homogeneous mixture of gases. This movement takes place in opposition to gravity since hydrogen which is a lighter gas moves downwards and the air which is a heavier gas moves upwards.

The process can be clarified with the help of another illustration. A glass-jar is filled with air and a coloured gas such as bromine is led at the bottom of the jar. It is found that bromine spreads uniformly throughout the entire space in the vessel. This means that although bromine is heavier than air, it has moved upwards and penetrated the air

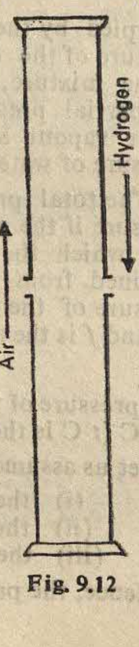


Fig. 9.12

to form a homogeneous mixture. In fig. 9.13, the upper vessel A is filled with hydrogen and the lower vessel B with carbon dioxide. The two vessels are connected by means of a tube provided with a stopcock. When the stopcock is opened, hydrogen moves downwards and carbon dioxide upwards, although carbon dioxide is 22 times denser than hydrogen. After few hours, a uniform mixture of two gases will be present in both the vessels. This phenomenon which is independent of gravity and is common to all gases is known as gaseous diffusion. *Diffusion is a process by which a gas spreads out and mixes spontaneously with other gases. The phenomenon of diffusion only takes place between gases which do not react chemically.* The process of diffusion occurs even when two gases are separated by a porous partition such as unglazed porcelain.

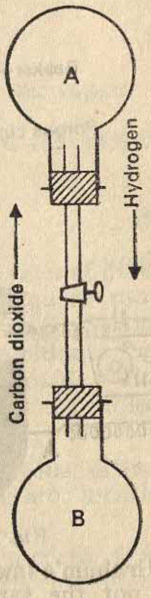


Fig. 9.13

If sulphuretted hydrogen gas is allowed to escape from a Kipp's apparatus placed in one corner of a room, the gas spreads uniformly throughout the entire space of the room within a very short time by diffusion and the bad smell of the gas is felt in very part of the room.

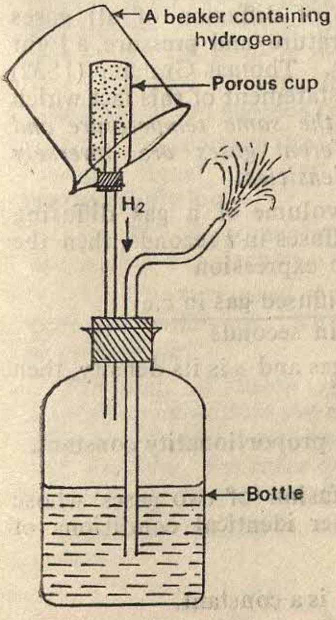


Fig. 9.14

Experiments illustrating the phenomenon of gaseous diffusion. Experiment—I. A porous cup is filled with air and attached to a bottle provided with a fine nozzle (fig. 9. 14). The bottle contains water. If a large beaker is filled with hydrogen and lowered over the porous cup, water will be vigorously forced out of the nozzle. The explanation is simple. Hydrogen from the beaker diffuses into the cup more rapidly than the slower moving air diffuses out. Hence, more gas enters the cup than leaves the cup. This increases the pressure inside the bottle, which causes water to be forced out of the nozzle.

Experiment—II. A U-tube is filled with mercury as shown in figure 9.15. One limb of the tube is connected with a porous cup which contains air. The two platinum wires A and B are fused with the other limb of the tube and are connected to an electric bell. The platinum wire A is in contact with mercury while B is just above it. If a gas-jar or a beaker filled with hydrogen is inverted over the porous cup, the electric bell starts ringing. The explanation of this phenomenon is that hydrogen diffuses more rapidly into the porous cup than air diffuses out. This causes the pressure of the gas to increase in right limb and mercury level in the left limb rises. The circuit is thus completed and the bell starts ringing.

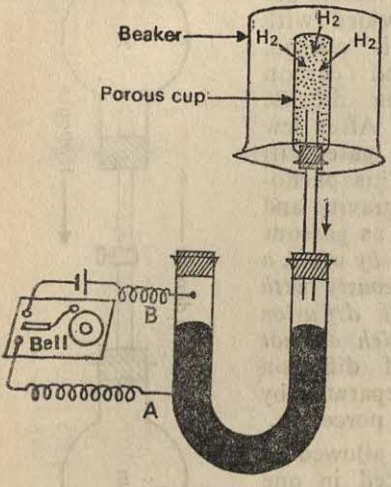


Fig. 9.15

Marsh gas detector by which dangers in coal mines are avoided works on the same principle.

Graham's law of diffusion. The rate of diffusion of all gases are not the same. At a given temperature and pressure, a light gas diffuses more rapidly than a heavy gas. Thomas Graham (1832) was the first to make a quantitative statement of this fact which is now known as Graham's law. *At the same temperature and pressure, the rates of diffusion of different gases are inversely proportional to the square roots of their densities.*

The rate of diffusion is defined as the volume of a gas diffusing per unit time. Thus, if v c.c. of a gas diffuses in t seconds, then the rate of diffusion of the gas is given by the expression

$$r = \text{rate of diffusion} = \frac{v}{t} = \frac{\text{volume of diffused gas in c.c.}}{\text{time in seconds}}$$

If r is the rate of diffusion of a gas and ρ is its density, then at a specified temperature and pressure

$$r \propto \frac{1}{\sqrt{\rho}} \quad \therefore \quad r = \frac{k}{\sqrt{\rho}}$$ where k is a proportionality constant.

If r_1 and r_2 represent the rates of diffusion of two gases whose densities are ρ_1 and ρ_2 respectively under identical conditions of temperature and pressure, then

(i) $r_1 \propto \frac{1}{\sqrt{\rho_1}}$ or, $r_1 = \frac{k}{\sqrt{\rho_1}}$ where k is a constant.

(ii) $r_2 \propto \frac{1}{\sqrt{\rho_2}}$ or, $r_2 = \frac{k}{\sqrt{\rho_2}}$

Hence, $\frac{r_1}{r_2}=\frac{k}{\sqrt{\rho_1}}\times\frac{\sqrt{\rho_2}}{k}=\sqrt{\frac{\rho_2}{\rho_1}}$ which is the mathematical form of Graham's law. (9·31)

Again, $\frac{r_1}{r_2}=\sqrt{\frac{\rho_2}{\rho_1}}=\sqrt{\frac{D_2}{D_1}}$ where D_1 and D_2 are the vapour densities of the two gases. Hence, if M_1 and M_2 are the molecular weights of the two gases, then

$$\frac{r_1}{r_2}=\frac{v/t_1}{v/t_2}=\frac{t_2}{t_1}=\sqrt{\frac{D_2}{D_1}}=\sqrt{\frac{M_2}{M_1}} \tag{9.32}$$

Hence, at the same temperature and pressure, the rates of diffusion of different gases is inversely proportional to the square roots of their molecular weights. Hence, hydrogen sulphide (H_2S) diffuses more rapidly than sulphur dioxide (SO_2) because molecular weight of hydrogen sulphide is less than that of sulphur dioxide. Hence, by applying Graham's law it is possible to determine the molecular weights of gases.

Practical applications of the phenomenon of gaseous diffusion. Some practical applications of gaseous diffusion are mentioned below :

(1) A technique based on gaseous diffusion is used to separate the isotope of uranium which is used for the construction of atomic bomb. This isotope is present in natural uranium to the extent of 0·7%. This is separated from natural uranium by successive diffusions of the gaseous compound, uranium hexafluoride.

(2) The construction of "marsh gas detector" which is used as "danger signal" in coal mines is based on the phenomenon of gaseous diffusion.

(3) The phenomenon can be extended to determine the relative densities and molecular weights of gases.

(4) The two gases of different densities may be separated by the process of diffusion. This process of separation of gases is known as *atomolysis*.

Effusion. *Effusion is a process by which a gas is forced through a small aperture into the air.* Graham's law is also applicable to the effusion of gases and can be stated as : *At a constant temperature and pressure, the rates of effusion of different gases are inversely proportional to the square root of their densities.*

Since the molecular weight of a gas is twice the relative density, we have

$$\frac{r_1}{r_2}=\sqrt{\frac{\rho_2}{\rho_1}}=\sqrt{\frac{M_2}{M_1}} \tag{9·33}$$

where M_1 and M_2 are the molecular weights of the two gases. From equation (9·33), it is evident that the molecular weights of different gases can be compared provided the rates of effusion are determined exprimentally.

Bunsen's Effusiometer. The apparatus (shown in fig. 9·16) consists of a graduated tube G fitted with a stop-cock. A platinum plate P having a very fine aperture is sealed into the mouth of the graduated tube. The tube is placed in a cylinder filled with water (when the gas is soluble in water, mercury is used) and the temperature is indicated by the thermometer T. One of the two gases is admitted into the graduated tube until the water in G is forced down to the graduation mark B. The stop-cock is then opened. The gas effuses into the air through the aperture in the platinum plate under the pressure of the displaced water. The time taken for the water level in the graduated tube to rise to the mark A is noted. The experiment is then repeated with another gas.

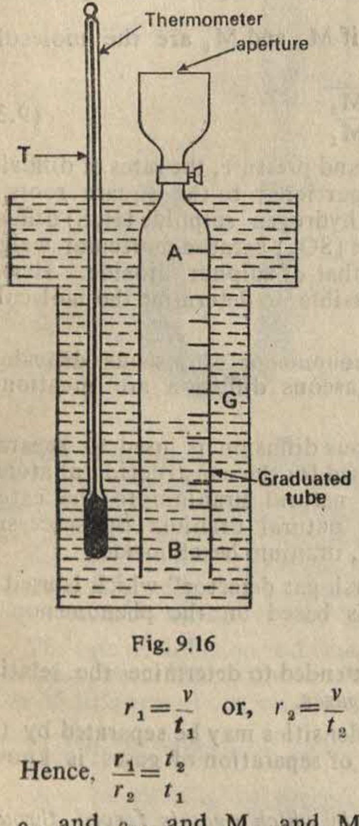


Fig. 9.16

Let us suppose that t_1 and t_2 are the observed times in which equal volumes, v of the two gases effuse. If r_1 and r_2 are the rates of effusion, then

$$r_1=\frac{v}{t_1} \quad \text{or,} \quad r_2=\frac{v}{t_2}$$

Hence, $\dfrac{r_1}{r_2}=\dfrac{t_2}{t_1}$ (9·34)

If ρ_1 and ρ_2, and M_1 and M_2 are the densities and molecular weights of the two gases respectively, then from (9·33) and (9·34)

$$\frac{r_1}{r_2}=\frac{t_2}{t_1}=\sqrt{\frac{\rho_2}{\rho_1}}=\sqrt{\frac{M_2}{M_1}}$$

If molecular weight of one gas is known, then that of the other can be determined.

Problems

Ex. 1. At a given temperature, the pressure of a gas occupying a volume of 2 litres is 600 mm of Hg. What will be the pressure if the volume is reduced to 1·5 litres without changing the temperature?

Let the pressure be P_2, then the data given in the problem can be represented as

$P_1=600$ mm of Hg.

$V_1=2$ litres ; $V_2=1{\cdot}5$ litres ; $P_2=?$

By Boyle's Law, $P_1V_1=P_2V_2$

$$\text{Hence, } P_2=\frac{P_1V_1}{V_2}=\frac{600 \text{ m.m.}\times 2 \text{ litres}}{1{\cdot}5 \text{ litres}}=800 \text{ m.m. of Hg.}$$

(The students should use the units of the variables in addition to their numerical values. The units can be multiplied and divided in the same manner as the numbers).

Ex. 2. A sample of air occupies a volume of 300 ml. at 25°C. If the pressure is maintained constant, what will be the temperature at which the volume of the same sample of air is 270 ml. ?

Solution. Let the temperature be T_2°K. Then the data presented in the problem can be tabulated as :

$T_1=25^\circ C+273=298^\circ K$ $V_2=270$ ml.

$V_1=300$ ml. $T_2=?$

By Charles' law ; $\dfrac{V_1}{T_1}=\dfrac{V_2}{T_2}$

$$\text{or, } T_2=\frac{V_2\times T_1}{V_1}=\frac{270 \text{ ml.}\times 298 \text{ deg.}}{300 \text{ ml.}}=268{\cdot}2 \text{ deg. Kelvin.}$$

Now, $T_2=t_2+273$ where t_2 is the temperature in degree centigrade.

$=268{\cdot}2$ K

Hence, $t_2=-4{\cdot}8$ C.

Therefore, the final temperature is $-4{\cdot}8$°C.

Ex. 3. 400 ml. of hydrogen were collected over water at 40°C and at 750 mm. pressure. What will be the volume of dry hydrogen at N.T.P. ? (partial pressure of water vapour at 40°C=55 mm of Hg.)

Solution. $P=P_{H_2}+P_{H_2O}$ where P=total pressure of the mixture.

Hence, $P_{H_2}=P-P_{H_2O}=750-55=695$ mm of Hg.

Let us designate the volume of dry hydrogen by V_2 at N.T.P.

Then we apply the general gas equation $\dfrac{P_1V_1}{T_1}=\dfrac{P_2V_2}{T_2}$

$P_1=695$ mm of Hg. $P_2=760$ mm of Hg.

$V_1=400$ ml. $V_2=?$

$T_1=40+273=313^\circ K$ $T_2=0+273=273^\circ K$.

$$\text{Hence, } V_2=\frac{V_1P_1T_2}{T_1P_2}=\frac{400 \text{ ml.}\times 695 \text{ mm of Hg.}\times 273 \text{ deg. Kelv.}}{313 \text{ deg. Kelvin}\times 760 \text{ mm of Hg.}}$$

$=319{\cdot}0$ ml.

Ex. 4. A quantity of a gas A exerts a pressure of 520 mm of Hg in a volume of 2 litres. Another gas B exerts a pressure of 610 mm of Hg in a volume of 3 litres. Another gas C exerts a pressure 580 mm of Hg in a volume of 5 litres. If the gases are placed in 10-litre container, what will be the total pressure and the partial pressure of each gas ?

Solution. First partial pressures of individual gases are determined.

For gas A. Let P_A be the partial pressure of the gas. Then by Boyle's law : $P_1V_1=P_AV_2$

or $P_A=\frac{P_1V_1}{V_2}$

$P_1=520$ mm of Hg ; $P_A=?$
$V_1=2$ litres. $V_2=10$ litres.

Hence, $P_A=\frac{520 \text{ mm of Hg}\times 2 \text{ litres}}{10 \text{ litres}}=114$ mm of Hg.

Similarly, $P_B=$ partial pressure of the gas B.

$$=\frac{610 \text{ mm of Hg.}\times 3 \text{ litres.}}{10 \text{ litres.}}=183 \text{ mm of Hg.}$$

and $P_C=\frac{580 \text{ mm of Hg.}\times 5 \text{ litres.}}{10 \text{ litres.}}=240$ mm of Hg.

By Dalton's law, the total pressure of the mixture is given by

$$P=P_A+P_B+P_C$$
$$=114+183+240=537 \text{ mm of Hg.}$$

Ex. 5. A mixture of gases contains 40 per cent of oxygen and 60 per cent of hydrogen. The pressure of the mixture is 600 mm. of Hg. Calculate the partial pressure of each gas separately.

Solution : Since the partial pressure of a gas is proportional to the gas content (*v*/*v*) of a mixture, 600 mm should be divided proportionally to 40 and 60.

Hence, $P_{O_2}=$ partial pressure of oxygen

$$=\frac{600\times 40}{100}=240 \text{ mm. of Hg.}$$

$$P_{H_2}=\frac{600\times 60}{100}=360 \text{ mm. of Hg.}$$

Ex. 6. A spherical balloon of 21 cm. diameter is to be filled up with helium at N.T.P from a cylinder containing the gas at 27·753 atmospheres and 27°C. If the cylinder can hold 4 litres of water, calculate the number of balloons that can be filled up.

Solution : The radius of the spherical balloon $=\frac{21}{2}$ cm.
volume of the balloon $=\frac{4}{3}\pi r^3$

$$=\frac{4}{3}\times\frac{22}{7}\times\left(\frac{21}{2}\right)^3=4851 \text{ c.c}$$

volume of the cylinder $=4000$ c.c

Hence, the amount of the gas which the cylinder can hold at 27 C and 27·753 atm=4000 c.c

$$\therefore \text{ the volume of helium at N.T.P.} = \frac{4000 \times 27{\cdot}753 \times 273}{300 \times 1}$$

$$\simeq 101020{\cdot}9 \text{ c.c}$$

Of this total volume, 4000 c.c of helium at 1 atmosphere remains in the cylinder. Hence, the amount of the gas available for filling the balloon is 101020·9 − 4000=97020·9 c.c.

$$\text{Therefore, the number of balloons} = \frac{97020{\cdot}9}{4851} \simeq 20$$

Ex. 7. At N. T. P. 400 c. c. of hydrogen diffuse through a small opening in 10 seconds and 40 c.c. of oxygen diffuse through the same opening in 4 seconds. If the density of hydrogen at N.T.P. is 0·0899 gm. per litre, calculate the density and molecular weight of oxygen. (mol. wt. of $H_2=2$).

r_{H_2}=rate of diffusion of hydrogen$=\frac{400}{10}=40$ c.c. per second.

r_{O_2}=rate of diffusion of oxygen$=\frac{40}{4}=10$ c.c. per second.

By Graham's law

$$\frac{r_{H_2}}{r_{O_2}} = \sqrt{\frac{d_{O_2}}{d_{H_2}}} = \sqrt{\frac{M_{O_2}}{M_{H_2}}}$$

$$\frac{40}{10} = \sqrt{\frac{d_{O_2}}{0.0899 \text{ gm/litre}}}$$

$$\text{or, } \frac{d_{O_2}}{0.0899 \text{ gm/litre}} = 16 \quad \therefore \; d_{O_2} = 16 \times 0{\cdot}0899 \text{ gm/litre}$$

$$= 1{\cdot}4384 \text{ gm/litre.}$$

$$\text{Again, } 4 = \sqrt{\frac{M_{O_2}}{2}} \qquad \text{or, } M_{O_2} = 16 \times 2 = 32$$

Hence, the density and molecular weight of oxygen are 1·4384 gram/litre and 32 respectively.

Ex. 8. A mixture of nitrogen and helium contains 80% by volume of nitrogen. 20 grams of the mixture are stored in a 5-litre vessel at 27°C. Calculate the partial pressures of the gases. The density of the mixture at N.T.P. is 2 grams per litre.

Solution : The volume of the mixture at N.T.P.$=\dfrac{20 \text{ grams}}{2 \text{ grams/litre}}$

$$= 10 \text{ litres.}$$

Let P be the total pressure of the mixture.

Hence, the volume of the mixture at 27°C and at P mm. of Hg is 5 litres. By combined gas laws,

$$\frac{\text{P} \times 5 \text{ litres}}{(273+27)^\circ\text{K}} = \frac{760 \text{ mm. of Hg.} \times 10 \text{ litres}}{273^\circ\text{K}}$$

$$\text{or,} \quad \text{P} = \frac{760 \text{ mm. of Hg} \times 10 \text{ litres} \times 300^\circ\text{K}}{273^\circ\text{K} \times 5 \text{ litres.}}$$

$$= 1670{\cdot}3 \text{ mm. of Hg.}$$

$$\text{Volume of nitrogen at } 27^\circ\text{C} = \frac{80 \times 5 \text{ litres}}{100} = 4 \text{ litres.}$$

$$\text{Volume of helium at } 27^\circ\text{C} = \frac{20 \times 5 \text{ litres}}{100} = 1 \text{ litre.}$$

$$\text{Hence, the partial pressure of nitrogen} = \frac{4 \text{ litre}}{5 \text{ litre}} \times 1670{\cdot}3 \text{ mm. of Hg.}$$

$$= 1336{\cdot}24 \text{ mm. of Hg.}$$

$$\text{the partial pressure of helium} = \frac{1 \text{ litre}}{5 \text{ litre}} \times 1670{\cdot}3 \text{ mm. of Hg.}$$

$$= 334{\cdot}06 \text{ mm. of Hg.}$$

Ex: 9. Assume the centre of the sun to consist of gases whose average molecular weight is 2·0. The density and pressure of the gases are 1·3g/c.c. and $1{\cdot}12 \times 10^9$ atmosphere respectively. Calculate the temperature of the sun. [I. I. T., '66.]

Solution. The volume occupied by 2 grams of the gases, i.e., 1 gm-molecular weight, i. e., 1 mole of the gase is

$$\text{V} = \frac{2 \text{ gm}}{1{\cdot}3 \times 1000 \text{ gm/litre}} = 1{\cdot}539 \times 10^{-3} \text{ litre.}$$

For 1 mole of the gases, the equation of state is

$$\text{PV} = \text{RT} \quad \therefore \quad \text{T} = \frac{\text{PV}}{\text{R}}$$

$$\therefore \text{T} = \frac{1{\cdot}12 \times 10^9 \text{ atm.} \times 1{\cdot}539 \times 10^{-3} \text{ litre}}{0{\cdot}082 \text{ litre-atm./deg. abs.}} = 21{\cdot}02 \times 10^6 \text{ deg. abs.}$$

Ex. 10. An open vessel at 27°C is heated until three-fifths of the air in it has been expelled. Assuming that the volume of the vessel remains constant, find the temperature to which the vessel has been heated. [I. I. T., '77]

Let T°K be the temperature at which three-fifths of the air in the flask is expelled. Let V be the volume of the flask. The volume of the expelled air is $\frac{3}{5}$V. Hence, V on expansion becomes $\text{V} + \frac{3}{5}\text{V} = \frac{8}{5}\text{V}$.

$$\frac{\text{P} \times \text{V}}{27+273} = \frac{\frac{8}{5}\text{V} \times \text{P}}{\text{T}} \quad \text{or,} \quad \text{T} = 480^\circ\text{K} = 207^\circ\text{C}$$

$$\therefore \text{Temperature} = 207^\circ\text{C}$$

Ex. 11. 40 c.c. of oxygen measured at N.T.P. were confined in a tube of cross-section 7·2 sq. cm. sealed at upper end, and standing in a trough of mercurry, the column of which stood at a height of 15·6 cm. The pressure of the atmosphere was found to be 756 mm and the temperature of the laboratory was 31°C. Calculate the length of the tube containing the gas. [C. U., '41]

Let the volume of oxygen inside the tube be Vc.c.

Pressure of oxygen inside the tube $=756-156=600$ mm.

Temperature of oxygen inside the tube $=31+273=304$ K

$P=760$ mm $\qquad P_1=600$ mm

$T=273°K$ $\qquad T_1=304°K$

$V=40$ c.c. $\qquad V_1=?$

$$\frac{PV}{T}=\frac{P_1V_1}{T_1} \quad \therefore \quad V_1=\frac{PVT_1}{P_1T}=\frac{760\times40\times304}{600\times273}=56\text{·}42 \text{ c.c.}$$

Let l cm. of the tube be filled with the gas. Then

$l\times1\text{·}2=56\text{·}42 \quad \therefore \quad l=47$ cm.

Ex. 12. At what depth in a pond will a bubble of air have one half of the volume it will have on reaching the surface ? Given that barometric height $=76$ cm., density of mercury $=13\text{·}6$, and temperature of water in the pond $=15°C$.

Let the volume of the bubble at the surface $=V$ c.c. $\therefore$ Its volume below the surface of water $=\frac{V}{2}$ c.c. By Boyle's law, we have

$76\times V=P_1\times\frac{V}{2}$ where P_1 = pressure on air bubble below the surface of water.

$\therefore \quad P_1=76\times2=152$ cm. of Hg.

$\therefore$ Pressure on air bubble below the surface of water
= atmospheric pressure (76 cm. Hg.) + pressure of water.

$\therefore$ Pressure of water on the air bubble $=(152-76)=76$ cm. of Hg.

Hence, the air bubble was $76\times13\text{·}6=1033\text{·}6$ cm. below the surface of water.

Ex. 13. There is an open bottle of air at 27°C. To what temperature must the bottle be subjected so that the number of molecules in the bottle (i) increase by 50% and (ii) decrease by 50% ? Assume that the volume of the bottle remains constant.

Let the number of molecules present in the bottle at 27°C be n.

(i) Let us suppose that at T_1°K the number of molecules increases to $(n+\frac{1}{2}n)$ or $\frac{3}{2}n$. Since the bottle is open, the pressure (P) remains constant. Hence, $PV=\frac{n}{N}R(27+273)=\frac{3n}{2N}RT_1$

[V=volume of the bottle and N=Avogadro number]

$\therefore\ T_1=200^\circ K$

(ii) Let us suppose that at $T_2{}^\circ K$ the number of molecules decrease to $(n-\frac{1}{2}n)$ or $\frac{1}{2}n$. Hence,

$$PV=\frac{n}{N}R(27+273)=\frac{n}{2N}RT_2$$

$$\therefore\ T_2=600^\circ K.$$

EXERCISE

1. State Boyle's law, Write equation for it. Describe an experiment by which you can verify the law.

2. State Charles' law and Graham's law, Give the mathematical expression for (a) the law of Charles, (b) the law of Boyle, and (c) Graham's law.

3. Establish a relation between temperature, pressure and volume of a gas. How would you proceed practically to show the effect of change of temperature on the volume of a gas?

4. When T is constant show that the equation $P_1V_1/T_1=\frac{P_2V_2}{T_2}$ reduces to the law of Boyle.

5. When P is constant show that the equation $P_1V_1/T_1=P_2V_2/T_2$ reduces to the law of Charles.

6. What is meant by the term "perfect or ideal gas"? Deduce the ideal gas equation $Pv=nRT$.

7. Deduce a relation between the density and pressure for a given mass of gas at constant temperature.

8. Deduce a relation between density and temperature for a given mass of gas at constant pressure.

9. What is meant by "standard conditions". Write notes on (a) ideal gas (b) real gas.

10. By means of examples show what is meant by "partial pressure". State Dalton's law of partial pressure. What is aqueous tension?

11. Explain clearly the phenomenon of diffusion and effusion. State Graham's law of diffusion. Describe an experiment to show that hydrogen diffuses more rapidly than carbon dioxide.

12. Discuss the meaning of the absolute temperature.

13. State whether each of the following pairs of variables relating to gases represent direct or inverse proportion.

(a) P and V (T and M constant)
(b) V and T (P and M constant)
(c) P and T (V and M constant)
(d) d and P (T and M constant)

14. Give one everyday application of (a) Boyle's law (b) Charles' law and (c) Phenomenon of diffusion.

15. Establish the relation between temperature, pressure and volume of a given mass of a gas. Explain the difference between the equations $PV=RT$ and $Pv=nRT$.

16. With the help of the gas laws, prove that $Pv=nRT$. Express the value of R in different units.

17. What do you mean by ideal gas and real gas? How is the molecular weight of a gas determined from ideal gas equation?

18. How would you determine the molecular weight of a gaseous compound by the combination of Boyle's law, Charles' law and Avogadro's law?

19. What do you mean by partial pressure of a gas? State Dalton's law of partial pressure. Deduce a relation between partial pressure and mole fraction of a gas in a mixture. How would you determine the pressure of a gas collected over water?

20. What do you mean by diffusion and effesion of a gas? State Graham's law of diffusion. Give the mathematical formulation of the law. What are the applications of diffusion?

21. What is effusion? How would you determine the molecular weight of a gas by using effusion?

22. Show a graphical representation of a gas obeying Boyle's law with volume along X-axis and pressure along Y-axis.

23. What will be the nature of the graph when

(a) PV is plotted against V at constant temperature.
(b) PV is plotted against P at constant temperature.
(c) V is plotted against T at constant pressure.
(d) P is plotted against T(°K) at constant volume.
(e) V is plotted against t (°C) at constant pressure.
(f) rate of diffusion against square root of density at constant temperature.
(g) P is plotted against $\frac{1}{V}$ at constant temperature.

24. Which one of the following pair of gases has higher rate of diffusion.

(i) O_2, SO_2, (ii) CO_2, SO_2 and (iii) $^{235}_{92}U\ F_6$, $^{238}_{92}U\ F_6$

Problems

1. A certain mass of gas occupies a volume of 100 ml. at a pressure of 3 atm. At what pressure will it occupy a volume of 200 ml., if the temperature remains constant? [Ans. 1·5 atm.]

2. At 27°C the volume of a given mass of gas is 1000 ml. Keeping the pressure constant, what would be the volume of the gas if placed in a room at 0°C? [Ans. 910 ml.]

3. If the density of helium is 16 at 730 mm. pressure, what will be its density when the pressure is doubled? [Ans. 32]

4. The density of nitrogen is 14 under 760 mm. of Hg and at a certain temperature. At what pressure will the density become 10, if the temperature is kept constant? [Ans. 542·8 mm. of Hg.]

5. The density of oxygen is 16 at 0°C. If the pressure is kept constant, what will be the density of oxygen at −10°C? [Ans. 16·608]

6. A certain quantity of gas occupies a volume of 2 litres at N.T.P. What will be its volume at 740 mm. of Hg. and 23°C ? [Ans. 2·26 litres appx.]

7. An automobile tire is inflated to a pressure of 30 lb/sq. inch on a summer morning when the temperature is 22°C. What will be the pressure in the same tire at noon when the temperature is 37°C ? [Ans. 31·53 lb/inch.^{2}]

8. A certain quantity of a gas was collected over water at 27°C and 750 mm. pressure and measured 250 ml. What will be the volume of the dried gas at 60°C and 800 mm. pressure ? Aqueous tension at 27°C is 26·75 mm. of Hg. [Ans. 250·8 ml.]

9. 152 ml. of a gas was collected over water in a jar at 25°C. The height of water level in the jar above that in the trough is 4·08 mm. and the barometric reading is 771·8 mm. of Hg. What volume will the dry gas occupy at N.T.P. ? Partial vapour pressure of water is 23·8 mm. of Hg. and the density of mercury is 13·6 gram per ml. [Ans. 136·5 ml.]

10. Calculate the volume of one mole of a gas at a temperature of 27°C and a pressure of 600 mm. [Ans. 31·183 litres.]

11. 1 litre of oxygen at N.T.P. weighs 1·43 gram. Determine the weight of 608 ml. of oxygen at 25°C and a pressure of 745 mm. of Hg. [Ans. 0·78 grams]

12. 3·5 litres of carbon dioxide weighs 6·88 grams at N.T.P. Calculate its molecular weight. [Ans. 44 gram]

13. Determine the volume occupied by 5·25 grams of nitrogen at 26°C and a pressure of 736 mm. of Hg. [Ans. 4·75 litres]

14. An observation balloon occupies 10,000 litres when at sea level and at 27°C. Calculate the increase in volume when it rises to a height of 8 miles when the temperature is −33°C and pressure is $\frac{3}{5}$ atmosphere. [Ans. 3333·3 litres]

15. A cylinder of nitrogen contains 100 litres of the gas under a pressure of 100 atmospheres. Calculate the number of gas jars each of 1 litre capacity which could be filled up from the cylinder when the atmospheric pressure is 760 mm. of Hg. [Ans. 9900]

16. 3·5 grams of potassium chlorate when heated gave off 300 c. c. of oxygen at 27°C and 767·5 mm.of Hg. The gas was collected over water. If partial vapour pressure of water at 27°C is 17·5 mm. of Hg. what volume of dry oxygen at N.T.P. would be given off by 2 grams of potassium chlorate ? [Ans. 153·8 ml.]

17. A balloon is descended to $\frac{3}{4}$th of its maximum stretching capacity and occupies a volume of 900 c.c. at 27°C. What is the maximum temperature above which it will burst ? [Ans. 127°C.]

18. A volume of gas together with a crystal of calcite measures 150 c.c. at 760 mm. of Hg. When the pressure is increased to 1000 mm., the combined volume becomes 116·4 c.c. Calculate the volume of the crystal. [Ans. 10 c.c.]

19. Air contains 21 per cent of oxygen (by volume). What is the partial pressure of oxygen in the air at standard pressure ? [Ans. 159·6 mm. of Hg.]

20. A gaseous mixture consists of nitrogen monoxide and nitrogen dioxide. Calculate the volume per cent content of the gases in the mixture if their partial pressures are 300 and 500 mm. of Hg respectively. [Ans. 37·5% and 62·5%]

21. At N.T.P. one litre of methane weighs 0·7168 gram/litre and one litre of sulphur dioxide weighs 2·927 gram/litre. Calculate the relative rates of diffusion of the two gases. [Ans. 2 : 1.]

22. 400 c.c. of carbon dioxide, 300 c.c. of oxygen and 500 c.c. of nitrogen are mixed. Pressure of carbon dioxide before mixing was 520 mm. of Hg., oxygen pressure was 600 mm. of Hg and nitrogen pressure 420 mm. of Hg. The volume of the mixture is 1 litre. Calculate the total pressure and partial pressure of each gas. [Ans. $P_{CO_2}=208$ mm. of Hg ; $P_{O_2}=180$ mm. of Hg.]
$P_{N_2}=210$ mm. of Hg ; $P=598$ mm. of Hg

23. The relative rates of diffusion of carbon dioxide and ozone were found to be 0·29 : 0·27. Calculate the density of ozone. (density of carbon dioxide = 22).
[Ans. 25·37] [Allahabad Inter Board, '46]

24. 500 c.c. of oxygen diffuse through a small aperture in 70 seconds. How long will it take 600 c.c. of chlorine to diffuse through the same aperture ?
[Ans. 210 seconds]

25. In a porous container, equal volumes of CH_4 and SO_2 are placed. After 20 minutes 800 c.c. of CH_4 had escaped. Calculate the volume of SO_2 that had escaped during the same period of time. [Ans. 400 c.c.]

[Mol. wt. of $CH_4 = 16$ and mol. wt. of $SO_2 = 64$]

26. 500 c.c. of a gas at 750 mm. of Hg. are passed into an evacuated flask of 700 c.c. capacity. Calculate the pressure in the flask.
[Ans. 535·65 mm. of Hg.]

27. The diameter of a soap bubble which contains air at 27°C and 730 mm. of Hg. is 6 cm. The bubble is expanded at constant temperature and pressure until its radius is 12 cm. Calculate the volume of air at N.T.P. required for the expansion. [Ans. 6128·9 c.c.]

28. 180 ml. of a hydrocarbon diffuse through a porous membrane in 15 minutes while 120 ml. of sulphur dioxide, under identical conditions, diffuse in 20 minntes. What is the molecular weight of the hydrocarbon. [Ans. 16]
[I. I. T., '71]

29. What will be the volume of 6 grams of hydrogen at 1·5 atmosphere and 273°C. [Ans. 89·544 litre] [I. I. T., '74]

30. 8 grams of methanol (CH_3OH) are vaporised in a 1-litre vessel at 127°C. What is the pressure inside the vessel ? [Ans. 8·2 atmosphere]

31. What will be the volume of 4·4 gram of carbon dioxide at 227°C and 10 atmosphere pressure ? [Ans. 0·41 litre]

32. What will be the pressure exerted by 4·4 gram of carbon dioxide inside a 1-litre vessel at 227°C ? [Ans. 4·1 atm.]

33. Find out the weight of nitrogen confined in a vessel of 100 c.c. capacity at 100 atmosphere pressure and at 227°C. [Ans. 6·832 gram]

34. Oxygen is collected over water in a vessel of 500 c.c. capacity at 27°C. Calculate the number of moles present in the gas if the total pressure of the gas at 27°C is 730 mm. and aqueous tension is 30 mm. of Hg. [Ans. 0·022 mole]

35. A gaseous hydrocarbon contains 25% hydrogen. The ratio of the rate of diffusion of hydrocarbon and hydrogen is $\sqrt{2} : 4$. Find the formula of hydrocarbon. [Ans. CH_4]

36. The time taken for a certain volume of oxygen containing 30% of ozone (by volume) to stream through a small hole is 170 seconds. Under exactly the same conditions, an equal volume of oxygen took 160 seconds. Calculate the density of ozone. [Ans. 22 875]

37. 48 c.c. of air take 36 seconds to diffuse out of a vessel. 42 c.c. of carbon dioxide take 39 seconds to diffuse out of the same vessel. If the vapour density of air is 14·4, calculate the vapour density of carbon dioxide. [Ans. 22·1]

38. When a mixture of oxygen and another gas is diffused, the resulting mixture contains 60% oxygen. Calculate the molecular weight of the gas.
[Ans. 72]

39. A compound exists in the gaseous state both as a monomer (A) and a dimer (A_2). The molecular weight of the monomer is 48. In an experiment, 96 gram of the compound was confined in a vessel of volume 33·6 litres and heated to 273°C. Calculate the pressure developed, if the compound exists as a dimer to the extent of 50 per cent by weight, under these conditions.

[Ans. 2 atm.] [I. I. T, '72]

40. At what depth in a pond will a bubble of air have $\frac{1}{3}$ of its volume? Barometric height is 76 cm. and the density of mercury is 13·6.
[Ans. 2067·2 cm.]

41. The height of mercury column in a barometer is found to be 76 cm. When 8 c.c. of oxygen at N.T.P. is collected over mercury in the barometer its volume is increased by 2 c.c. How much the mercury column is depressed?
[Ans. 152 mm.]

42. How many moles are present in 10 litre of a gas at 27°C and 10 atmosphere pressure?
[Ans. 4·065]

43. The density of a mixture of hydrogen and oxygen at 27°C and 740 mm. pressure is 2×10^{-4} gram/c.c. Calculate the percentage of oxygen (by weight) in the mixture.
[Ans. 65·6%]

44. 40 c.c. of hydrogen at N.T.P. were collected in a tube of cross-section 1·5 sq. cm. over mercury. The mercury level inside the tube was 14 cm. above the mercury level outside the tube. If the atmospheric pressure was 740 mm. of Hg and the temperature was 31°C find the length of the column of tube containing the gas.
[Ans. 37·6 cm.]

45. The weight of 56 c.c. of a diatomic gas at 2 atmosphere pressure and 0°C is 0·16 gram. Calculate the weight of one molecule of the gas.
[Ans. $2 \cdot 656 \times 10^{-23}$ gram]

CHAPTER X

SOLUTION AND SOLUBILITY

A mixture is composed of at least two separate substances existing in particles lying side by side. Each of the substances (or components) of a mixture retains its properties so that mixture can be separated into their components by physical methods. Mixtures can be divided into two classes : (i) heterogeneous mixture and (ii) homogeneous mixture. A mixture which is characterised by the dissimilarity of their parts, i.e., every part of which is not identical with every other parts is called a heterogeneous mixture. A mixture every part of which is identical with every other parts is called a homogeneous mixture. Homogeneous mixtures are commonly called solutions.

Solutions. Let us take a certain quantity of sugar into a beaker. Water is next added to it and stirred well. After some time, we shall not see any single crystal of sugar. The taste of the resulting mixture of sugar and water is now sweet. We describe the process by saying that sugar has been dissolved into water to form solution. The substance which dissolves another substance is called the solvent and the dissolved subtance is known as the solute. Here water is the solvent and sugar is the solute. An examination of the solution of sugar into water reveals that sugar is very uniformly distributed throughout water and the solution looks the same in all portions. That means that every part of it is identical with every other parts. Again, water can be separated from sugar by physical processes such as distillation in which water will be received as distillate and pure sugar will be left in the distilling flask. Hence, this solution is a mixture of sugar and water.

Again, if this solution is heated to a certain extent, some quantity of water will be lost by vaporisation. Then also we will be left with a solution of sugar and water. The quantity of sugar in the solution can also be varied to a certain limit. A solution can, therefore, be defined thus :

A solution is a homogeneous mixture of two or more substances such that their relative amounts may be gradually varied within certain limits.

In solution solvent is present in larger quantities and solute is present in smaller amount.

Solution is obtained by mixing solvent with solute, i.e.,

$$\text{solution} = \text{solvent} + \text{solute}$$

Now, if one mixes sand and water thoroughly, and permits the mixture to stand, the larger sand particles are observed to settle down quite rapidly and the smaller particles will take much longer time to settle down. Such mixtures are not homogeneous and are called suspensions. We describe the process by saying that sand is insoluble in water.

Saturated, unsaturated and supersaturated solutions. Let us take an average sized glass of water and a teaspoonful of sugar is added to it and stirred well. All sugars dissolve completely. If we add another teaspoonful of sugar, it also dissolves. When four or five teaspoonfuls are added, however, some sugars remain undissolved. It is evident, therefore, that at a definite temperature water will dissolve sugar upto a certain limit. When this limit is reached, water will no longer dissolve the sugar added and we say that the solution has reached the state of saturation.

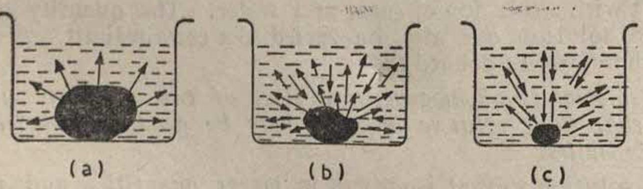
A solution is said to be saturated at a particular temperature when it will dissolve no more of the solute in which it is in contact. The dissolved and undissolved solids are said to exist in equilibrium in such a solution.

The state of saturation or equilibrium can be disturbed by incrasing or decreasing temperature. For example, if the saturated solution of sugar described above is heated, it will be found that the solution can now dissolve more sugar. It will be found further that larger and larger amounts of sugar will be required to make the solution saturated at higher and higher temperatures. Thus, a solution which is saturated at one temperature may not be saturated at another temperature.

A solution which will dissolve more solute when brought in contact with it is called unsaturated.

Let us explain with an example how the saturated and unsaturated solutions result :

If a lump of sugar is brought in contact with water at constant temperature, molecules of sugar detach from the surface of the solid and pass into solution. The rate of dissolution of sugar is highest initially. As the solution becomes concentrated, the dissolved molecules of sugar collide with the surface of the solid not yet dissolved and are attracted back to it and form part of its crystals (crystallisation). Since the concentration keeps increasing as the substance dissolves, the rate of crystallisation increases with time.



(a) (b) (c)

Fig. 10.1

while the rate of dissolution decreases with time. Finally, a moment arrives when both the rates become equal and a dynamic equilibrium is established. At this stage the concentration of the solution stops increasing and the solution becomes saturated.

That is, for any solution in which there is solid solute present, undissolved solid $\underset{v_b}{\overset{v_f}{\rightleftharpoons}}$ dissolved solid where v_f=rate of dissolution and v_b=rate of crystallisation. If $v_f=v_b$, the solution is saturated and if $v_f>v_b$ the solution is unsaturated.

The dissolving capacity of a solvent is not constant but varies with temperature ; the solvent will dissolve more solutes at higher temperatures. Thus, saturated solution at 90°C contains more solutes than the same solution saturated at 10°C. Hence, a saturated solution on being cooled deposits excess solutes until equilibrium is established at lower temperature. All saturated solutions, however, do not behave normally in that the expected separation of the solutes does not always occur immediately. If the saturated solution at the higher temperature contains no undissolved solute and no particles of foreign matter and if it is allowed to cool without being disturbed in any way, it is often possible to cool it without the separation of the expected solutes. A solution which has been so cooled obviously contains more dissolved solutes than the normal saturated solution at the existing temperature. Such a solution is said to be supersaturated and is in a metastable condition. A supersaturated solution may, therefore, be defined thus :

A solution is said to be supersaturated when it contains more solute in a given weight of solvent than is required to form a saturated solution at the same temperature.

If such solutions are disturbed by the addition of a tiny crystal of the solute or by any other means, the separation of excess of solute usually takes place rapidly until equilibrium is established.

Experiments demonstrating the phenomenon of supersaturation.

(1) Let us prepare a saturated solution of sodium sulfate at 30°C by dissolving sodium sulfate in water. If this solution is cooled to 15°C without making any disturbance, it is found that not a single crystal of excess sodium sulfate separates out. This solution at 15°C contains more sodium sulfate than the saturated solution of sodium sulfate prepared at 15°C. If a small crystal of sodium sulfate is introduced into the solution, excess of sodium sulfate separates out immediately.

(2) Another way of preparing supersaturated solution is to melt the crystals in its own water of crystallisation. A large test

tube is half filled with crystals of sodium thiosulfate (hypo). The neck of the test tube is plugged with cotton wool so that no dust particles can enter into the tube. The test tube is next gently heated when the salt melts in its own water of crystallisation forming a very concentrated solution. On cooling this solution, no solid crystallises or separates from it and the solution remains liquid. It is, therefore, a supersaturated solution.

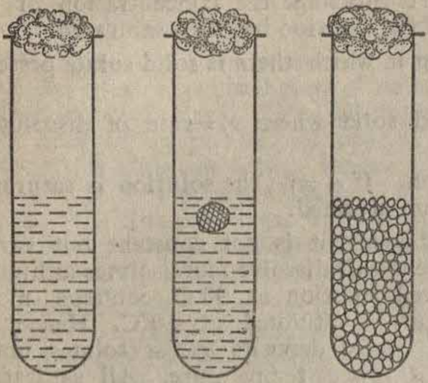


Fig. 10.2

Now the plug is removed and a small crystal of hypo is dropped into the liquid; the liquid at once begins to solidify with the evolution of heat.

So we conclude from the above experiments that *a supersaturated solution cannot remain supersaturated in contact with the solute.*

Tests of saturation, unsaturation and supersaturation. To test whether a solution of a substance is saturated, unsaturated or superasaturated at a particular temperature, a small crystal of the substance is introduced into the solution and the following observations are made :

(1) If the solute remains undissolved in contact with the solution, and the concentration of the solution remains the same, it is the saturated solution.

(2) If the solute dissolves either completely or partly and the concentration of the solution increases, it is the unsaturated solution.

(3) If the crystal of the solute grows in size and the concentration of the solution decreases, it is the supersaturated solution

Explanation of the act of dissolving. We can now offer an explanation for the act of dissolving. In general, polar solvents dissolve polar compounds, while non-polar solvents dissolve non-polar substances.

(i) When a crystal of sodium chloride is dropped into water, the ions at its surface begin to attract the polar water molecules. The water molecules are attracted to the sodium ions by their negative poles and to the chloride ions by their positive poles. The molecules of water then orient themselves around the sodium and chloride ions as shown in the figure 10.3. But the water molecules attract the ions with the same force as the ions attract the water molecules. As a result, the attraction between the ions is weakened so greatly that energy of motions of molecules in solution is enough to separate the ions from the crystal and make them pass into the solution. After the ions of the first layer has gone into the solution, the ions of the second layer pass into the solution. In this way, the crystal gradually dissolves. Such a process of dissolution is believed to occur in the case of ionic crystals.

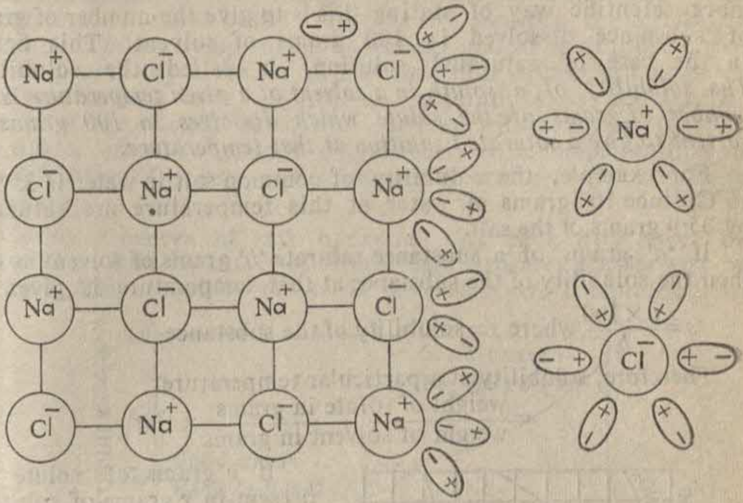


Fig. 10.3

(ii) Let us consider the case of a crystal of sucrose (table sugar) placed in a small beaker of water. Surface particles are held less firmly in the crystal structure than are interior ones. If the attraction between the molecules on the surface and water molecules is sufficiently strong, the surface molecules will be pulled from the crystal into water. The sucrose molecule contains a number of OH groups which are sufficiently polar to permit the development of strong attraction between the molecules of sucrose and water dipoles. This force of attraction is sufficiently strong to strip off the surface molecules of the crystal and make them pass into the solution. Due to diffusion, the stripped off molecules are distributed evenly throughout the bulk of the solution.

Such processes of dissolution would continue until all the solute present dissolved, were it not for the process, i.e., crystallisation occurring simultaneously. Due to erratic motions of the dissolved particles, some of them strike the undissolved portions of the crystals and remain to become a part of it again. Ultimately, a state of equilibrium will be reached in which the number of molecules going into the solution just equal the number returning to the solid state.

Solubility. Solutions are commonly called "strong" or "weak" according as they contain more or less dissolved substance. A more scientific way of stating this is to give the number of grams of substance dissolved in 100 grams of solvent. This figure, in the case of saturated solution, is called the solubility. *The solubility of a solute in a solvent at a given temperature is the number of grams of the solute which dissolves in 100 grams of solvent to give a saturated solution at that temperature.*

For example, the solubility of common salt in water is 35·9 at 15°C, since 100 grams of water at this temperature are saturated by 35·9 grams of the salt.

If '*a*' grams of a substance saturate '*b*' grams of solvent at t°C, then the solubility of the substance at that temperature is given by

$s=\frac{a\times 100}{b}$ where s=solubility of the substance.

Therefore, solubility at a particular temperature

$$=\frac{\text{weight of solute in grams}}{\text{weight of solvent in grams}}\times 100$$

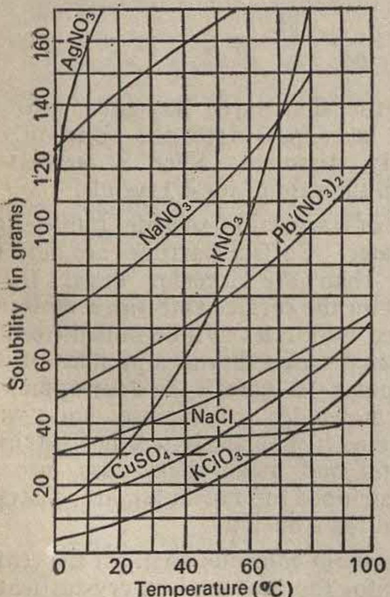


Fig. 10.4

If y grams of solute are present in x grams of solution at t C, then the solubility (at that temperature)$=\frac{y\times 100}{x-y}$

Many crystalline substances contain water of crystallisation and are called hydrates. Each hydrate has its own definite solubility, but in all cases the result is expressed in terms of salt free from water (anhydrous salt) contained in the solution per 100 grams of water. Solubility depends (i) on the chemical characters of the solute and solvent. For example, common salt is less soluble than "hypo" in water and both salts are nearly insoluble in alcohol. (ii) on the pressure ; this has very little effect except in the case of gases. (iii) on temperature ; generally solubility increases but not always, with rise of temperature.

Solubility curve. The change of solubility of a substance with temperature is most easily recorded by plotting the solubility (ordinate) against temperature (abscissa) and so obtaining a curve known as solubility curve. Fig. 10.4 shows the solubility curves of some substances in water at different temperatures. It appears that the solubilities of most substances increase with temperature ; the solubilities of a few change only slightly with temperature ; and the solubilities of a very small number decrease with increasing temperature.

Solubility curves of salt hydrates. (a) Solubility curve of borax. The solubility curves of several salt hydrates are shown in fig. 10.6. The solubility curves of these salts are complicated. In the solubility curve of borax ($Na_2B_4O_7$, $10H_2O$) there is a break at 61°C. Below 61°C the solubility of $Na_2B_4O_7$, $10H_2O$ increases with increase of temperature.

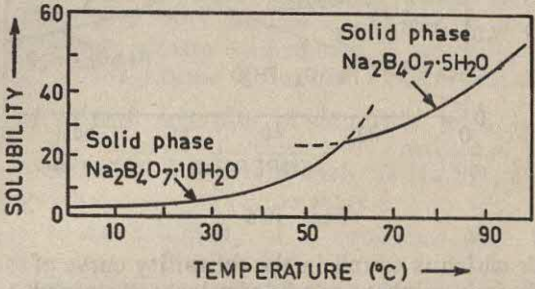


Fig. 10.5

Above 61°C, the decahydrate, $Na_2B_4O_7$, $10H_2O$ is dehydrated to pentahydrate, $Na_2B_4O_7$, $5H_2O$. Hence, the solubility curve which is obtained above 61°C is the solubility curve of the pentahydrate ($Na_2B_4O_7$, $5H_2O$) and the solubility curve which is obtained below 61°C is the solubility curve of the decahydrate. The two curves intersect at 61°C. For this reason, a break is found at 61°C in the solubility curve of borax.

(b) Solubility curve of hydrated calcium chloride. In the solubility curve of the hydrated calcium chloride two breaks are found ; one at 29·92°C and another at 45·5°C. Below 29·92°C, we get the solubility curve of the hexahydrate ($CaCl_2$, $6H_2O$). Above 29·92°C, the hexahydrate is dehydrated to the tetrahydrate ($CaCl_2$, $4H_2O$). Hence, the curve which is found above 29·92°C and below 45·5°C is the solubility curve of the tetrahydrate ($CaCl_2$, $4H_2O$). The curves of the hexahydrate and the tetrahydrate intersect at 29·92°C. For this reason, a break is found at 29·92°C. Above 45·5°C the tetrahydrate loses two molecules of water of crystallisation and is changed to dihydrate ($CaCl_2$, $2H_2O$). The solubility curve of the dihydrate is found above 45·5°C and this curve intersect the curve of the tetrahydrate at 45·5°C. Hence, we find another break at 45·5°C in the solubility curve of calcium chloride.

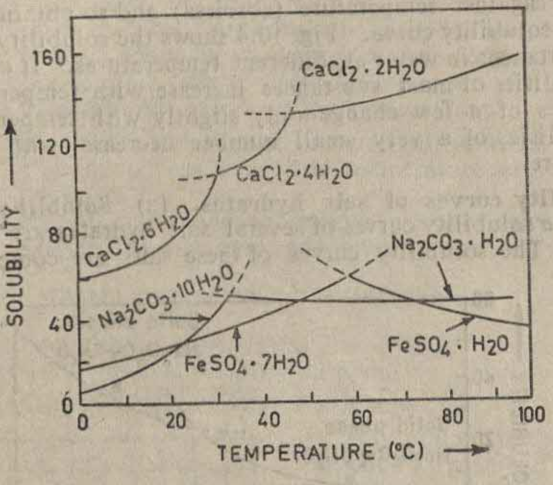


Fig. 10.6

The break which is found in the solubility curve of sodium carbonate and ferrous sulphate can be similarly explained.

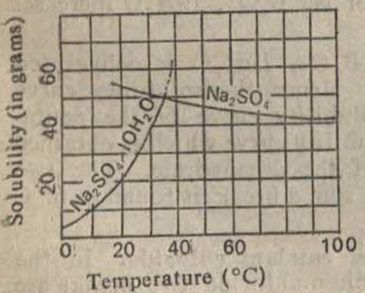


Fig. 10.7

(c) **Solubility curve of hydrated sodium sulphate.** A break is found in the solubility curve of hydrated sodium sulphate at 32·4°C. The curve which is found below 32·4°C is the solubility curve of the decahydrate (Na_2SO_4, $10H_2O$) and its solubility increases with increase in temperature. Above 32·4°C, the decahydrate is changed into anhydrous salt. Hence, the curve which is obtained above 32·4°C is that of the anhydrous sodium sulphate and its solubility decreases with increase in temperature. The curves of the decahydrate and the anhydrous sodium sulphate intersect at 32·4°C.

Utility of solubility curve. From the solubility curve, we learn the following :

(i) The concentration of a saturated solution at a given temperature.

(ii) The weight of solute which deposits from a solution of given concentration when it is cooled to a given temperature.

(iii) The order in which the substances separate out from a mixed solution under given conditions. Let a mixture of much potassium nitrate and little sodium nitrate be dissolved in hot water. It is desired to find which of the solutes will first separate out when this solution is cooled.

From solubility curve, it is seen that at about 70°C potassium nitrate and sodium nitrate have approximately the same solubility (viz., about 139 grams in 100 grams of water) but at 5°C the solubility of potassium nitrate has fallen to 17 grams per 100 grams of water, while the solubility of sodium nitrate remains at 77 grams per 100 grams of water. Now, from the definition of solubility it is evident that lower the solubility, faster the salt will separate out from the solution. So when the solution described above is cooled, potassium nitrate will first separate out since it has the lower solubility and sodium nitrate will remain in solution. This principle is the basis of the process of *fractional crystallisation.*

Explanation of the variation of solubility with temperature. The solubility of most salts increases with increase of temperature whereas the solubility of a few salts such as Na_2SO_4 and Na_2CO_3, H_2O decreases with increase of temperature.

The change in the solubility of a substance with temperature depends on its heat of solution.* If the heat is evolved on dissolving the substance in a solvent, the solubility of the substance decreases with increase of temperature. If heat is absorbed on dissolving the substance in its nearly saturated solution the solubility of the substance increases with increase of temperature.

A saturated solution in equilibrium with excess solute behaves according to Le Chatelier's principle.

solute (solid) $\rightleftharpoons$ solute (dissolved). If the temperature of such a system is raised, the equilibrium will shift, according to Le Chatelier's principle, in such a way as to tend to restore the system to its original temperature, by the absorption of heat from the reaction. If the heat is absorbed on solution, then with the increase of temperature more solute will dissolve and the system will be cooled with the absorption of heat. The system is then restored to its original temperature. The solibility of such substances increases with increase of temperature. If the heat is evolved on solution, then with increase of temperature, some solutes will come out of the solution and return back to the solid phase and the system will be cooled with absorption of heat to its original temperature. The solubility of such substances decreases with increase of temperature.

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* Heat of solution is defined as the amount of heat evolved or absorbed when one mole of a substance is dissolved in large excess of water, so that on further dilution of the solution no heat change is produced. If heat is absorbed when a substance dissolves in a solvent, then heat will be evolved when the solute comes out of the solution and returns back to the solid phase.

Measurement of solubilites. In order to find out the solubility of a substance, the first thing to be determined is the amount of the solute present in a saturated solution at a particular temperature. Let 'a' grams of the solute and 'b' grams of solvent are present in a saturated solution at temperature, t°C. By definition, the solubility of the substance at t°C is given by $s=\frac{a\times 100}{b}$ where s is the solubility of the substance. (10·1)

So the determination of 's' at t°C involves :

(i) preparation of saturated solution.

(ii) estimation of 'a' and 'b', i.e., the weights (in grams) of solute and solvent present in a saturated solution.

(a) Determination of the solubility of a substance at room temperature. Let us illustrate the principle of the method described above by determining the solubility of sodium chloride (common salt) in water at room temperature.

(i) Preparation of the saturated solution. Sodium chloride crystals are ground in a mortor and stirred with water for about 1 hour in a beaker till some of the salt remain undissolved. Thus is prepared the saturated solution of common salt in water.

(ii) Now a small evaporating basin made up of thin glass is weighed by a chemical balance. The saturated solution is filtered in the glass basin. The basin is next weighed with the solution. The solution is then evaporated to dryness on a water-bath when only common salt is left in the basin. The basin is then weighed. It is again dried in an air-oven and cooled in a desiccator and weighed again. The process is repeated till a constant weight of the basin with common salt is obtained.

Calculation. Let the weight of the empty glass basin$=W_1$ grams

The weight of the basin$+$salt solution$=W_2$ grams

The weight of the basin$+$salt left after evaporation$=W_3$ grams

$\therefore$ The weight of water$=(W_2-W_3)$ grams

The weight of salt$=(W_3-W_1)$ grams

Therefore, (W_2-W_3) grams of water and (W_3-W_1) grams of the salt are present in a saturated solution of common salt and water at room temperature. So by equation (10.1) the solubility 's' of common salt at room temperature is given by

$$s=\frac{(W_3-W_1)\times 100}{(W_2-W_3)}$$

(b) Determination of the solubility of a substance at a temperature higher than the room temperature. The solid is first powdered well and stirred for some time by a glass stirrer (driven by a motor) with water in a bottle which is supported in a thermostat (a thermostat is a water-bath maintained at a constant temperature by a thermoregulator). The contents of the bottle are brought to a desired temperature by regulating the temperature of the thermostat. Some of the clear saturated solution on the top are removed by a pipet and poured in a previously weighed dish and the dish with the solution is weighed again. The solution is now evaporated over a water-bath until nothing but a dry solid remains in the dish The dish and the solid are then weighed. The solubility of the solid is then calculated using these data by the method described above.

(c) Determination of the solubility of a solid at a temperature lower than the room temperature. First a saturated solution of a solid is prepared and taken in a big test tube. The test tube is fitted with a wider tube which is placed in a beaker containing ice. A thermometer is inserted into the solution of the test tube. Suppose that it is required to determine the solubility of the solid at 0°C. So when the thermometer reads zero degree centigrade, some of the clear saturated solution on the top are drawn off quickly and poured into a weighed dish The dish with the solution is weighed The solution is then evaporated to dryness and the dish with the dry salt is weighed again. From these data, the solubility of the solid at 0°C can be easily calculated.

The methods described above for the determination of solubility are not applicable to substances which are slightly soluble and which cannot be dried without decomposition.

Crystallisation. The process of crystallisation is based on the fact that a solution of a substance saturated at one temperature is not saturated at another temperature. Hence, if a saturated solution at higher temperature is cooled to a lower temperature, the excess solute is deposited. For example, if hot saturated solution of some common substances, e.g., alum, copper sulphate, sugar, table salt, etc., is allowed to cool, a quantity of each solute is thrown out of the solution. An examination of these deposited solutes shows that they consist of a number of small particles. These particles possess a definite geometrical shape and are bounded by perfectly plane faces. These particles are called *crystals*. The process by which these crystals are obtained is called crystallisation. Crystals are not only obtained from a state of solution but also obtained from a state of fusion or vapour.

The liquid left after crystals have separated out of it, is called the *mother liquor*.

Crystals. A solid possessing the following characteristics is said to be a crystal :

(i) *It should possess a definite geometrical shape and is bounded by perfectly plane faces. The angles between corresponding faces of all the crystals of a given substance are constant and are characteristics of that substance.*

(ii) *If a crystal is fractured, the new surfaces are plane, and are inclined to one another at angles which are constants and characteristic of the given substance.*

Solid substances are either crystalline or non-crystalline. Non-crystalline solids (i.e., having no crystalline shape) are called amorphous solids. Glass, pitch, etc., are examples of amorphous solids. Alum, common salt, sugar, etc., are examples of crystalline substances.

Crystalline substances break up easily along certain planes. For example, a piece of mica splits up into thin sheets ; rock salts break up easily into cubic or rectangular pieces when struck sharply and lightly. An amorphous solid, on the other hand, does not cleave along any particular plane when broken by a sharp blow but fractures with equal ease in any direction.

Fractional crystallisation. The process of fractional crystallisation is employed for the purification and separation of solids by making use of their different solubilities and particularly the fact that the solubilities of some substances increase more rapidly with rise of temperature than those of other salts. The theory of the process may, clearly, be understood from the inspection of the solubility curves. The following example will show how the process is carried out.

Let us take 50 grams of potassium chlorate in a porcelain dish. It is warmed for about ten to fifteen minutes at a temperature just above its melting point. The mass is then cooled. It contains undecomposed potassium chlorate, some potassium chloride and potassium perchlorate. About 50 c c. of hot water at 50°C is added to it when all three of the salts are dissolved to give a mixed solution of potassium perchlorate, potassium chlorate and potassium chloride. The solution is then evaporated until a drop crystallises when rubbed on a cold surface, and slowly cooled. The crystals of potassium perchlorate are the first to separate because it has the least solubility (the solubility at 15°C of potassium perchlorate, potassium chlorate and potassium chloride is 1.5 grams, 6.6 grams and 36 grams respectively). The first crop of crystals of potassium perchlorate is filtered off and redissolved and again allowed to

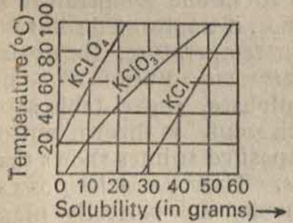


Fig. 10.8

crystallise by cooling the hot solution ; potassium perchlorate can thus be obtained almost free from other two salts. When the crystals of potassium perchlorate have been separated, the solution is further evaporated and allowed to cool. This time potassium chlorate is separated. These are filtered off and must be recrystallised in order to isolate a purer salt. The remaining mother liquor is then concentrated by evaporation, and cooled. Potassium chloride is separated out and similarly filtered and recrystallised. The process of recrystallisation has to be repeated several times in order to obtain the crystals in a high degree of purity.

The above operation is an example of fractional crystallisation. *The fractional crystallisation is the process in which only one of the solutes is allowed to crystallise from a solution of two or more different solutes having different solubilities.*

Water of crystallisation. Many substances while crystallising out of aqueous solution yield crystals containing definite amount of combined water. They take up this water from the solution during the process of crystallisation. The water molecules are loosely associated with the substance and are in a definite number. The crystalline shape of the substance depends upon these molecules of water and if these molecules of water are removed by some physical means such as heating, the substance loses its crystalline shape. The water thus associated with the crystal is known as *water of crystallisation* or *water of hydration.* The substances which contain water molecules combined in this manner in definite proportions are called *hydrates*. The same substances without the water of crystallisation are called *anhydrous*. The process of addition of water molecules as units to other substances is known as *hydration*.

If white anhydrous copper sulphate, $CuSO_4$, is dissolved in water, a blue solution results. On slow evaporation of the solution, blue crystals deposit. The chemical analysis of blue crystals reveals that there are five water molecules per molecule of copper sulphate. So copper sulphate with water as $CuSO_4, 5H_2O$ is known as hydrate. These five molecules of water are known as water of crystallisation or water of hydration and the process of taking up water molecules as units to copper sulphate crystals is known as hydration. Other common examples of salt hydrate are washing soda, $Na_2CO_3, 10H_2O$; oxalic acid, $H_2C_2O_4, 2H_2O$; green vitriol, $FeSO_4, 7H_2O$, etc.

It must be borne in mind that water is not an essential part of all crystals. There are certain substances which are crystalline in shape but do not contain water of crystallisation. Common salt, $NaCl$; potassium chloride, KCl ; potassium chlorate, $KClO_3$, etc., are the examples.

Experimental methods for the determination of water of crystallisation. The percentage of water of crystallisation can be determined for a large number of substances by strongly heating a weighed amount of the hydrated crystals and measuring the loss of weight. For example, when sodium carbonate is heated strongly, it loses only water of crystallisation and the residual anhydrous sodium carbonate remains unaffected by heat.

(a) Water of crystallisation of hydrated salts like calcium chloride, barium chloride, etc.

Experiment. A porcelain crucible with its lid is cleaned well. This is then heated strongly in a pipe-clay triangle and then cooled in a desiccator and weighed. The process of heating and cooling is repeated till the final weight is constant. This gives the weight of the empty crucible with its lid (W_1). A quantity of the crystals is then placed in the crucible and weighed again. This gives the weight of the crucible with its lid and hydrated salts (W_2). Now, the crucible is placed on the pipe-clay triangle, keeping the lid slightly open so as to allow the water of crystallisation to escape as steam. The crucible is carefully heated until nothing but a dry powder remains in the crucible. The crucible is then cooled in a desiccator and weighed. The heating and subsequent weighing are then repeated until a constant weight is obtained. This indicates that the salt has been completely dehydrated, i.e., all the water of crystallisation has been driven off. The last weight gives the weight of the crucible with its lid plus anhydrous salt.

Calculation. Let us suppose that

(i) weight of the empty crucible$+$lid$=W_1$ grams.

(ii) weight of the empty crucible$+$lid$+$hydrated salt$=W_2$ grams.

(iii) weight of the crucible$+$lid$+$anhydrous salt$=W_3$ grams.

$\therefore$ weight of the hydrated salt$=(W_2-W_1)$ grams.

weight of the anhydrous salt$=(W_3-W_1)$ grams and the weight of water of crystallisation

$$=(W_2-W_1)-(W_3-W_1)=W_2-W_1-W_3+W_1=(W_2-W_3)$$

grams.

Therefore, (W_2-W_1) grams of hydrated salt contain (W_2-W_3) grams of water of crystallisation.

$\therefore$ 100 grams of hydrated salt contain $\dfrac{(W_2-W_3)}{(W_2-W_1)}\times 100$ grams of water of crystallisation

$$\therefore \text{ Percentage of water of crystallisation}=\frac{(W_2-W_3)}{(W_2-W_1)}\times 100$$

Deduction of the formula of barium chloride crystal. Let us suppose that the formula of barium chloride is $BaCl_2$, n H_2O. It is required to find out the value of n. From the above analysis, we can write

$$\frac{\text{weight of anhydrous barium chloride}}{\text{weight of water of crystallisation}}$$

$$=\frac{1\times\text{molecular weight of barium chloride}}{n\times\text{molecular weight of water}}$$

i.e., $\frac{(W_3-W_1)}{(W_2-W_3)}=\frac{208\cdot3}{n\times18}$ [molecular weight of barium chloride is 208·3 and molecular weight of water is 18.]

The water of crystallisation in barium chloride crystals is 14·73%.

$$\therefore\ \frac{100-14\cdot73}{14\cdot73}=\frac{208\cdot3}{18\,n}$$

$\therefore$ n=2. Hence, the formula is $BaCl_2$, $2H_2O$.

Similarly, the formula of calcium chloride, etc., can be found out.

(b) The water of crystallisation of blue vitriol. The water of crystallisation of blue vitriol is determined by heating the crystals on a watch glass in an air-oven (air thermostat whose temperature can be regulated), because copper sulphate decomposes on strong heating in a direct flame.

A pair of watch glasses, held together by a clip, is weighed carefully. Some dry, pure and powdered copper sulphate are placed in the lower watch glass and the whole is weighed again. Now, the upper watch glass is slid little so that water of crystallisation can escape easily as steam. The pair of watch glasses with copper sulphate is placed in air-oven whose temperature can be regulated and is heated at 250°C for about 15 minutes. The pair of watch glasses with the anhydrous salt is cooled in a desiccator and weighed carefully with the clip. The heating and subsequent weighing are then repeated until a constant weight is obtained.

Calculation. The above experimental results can be represented as follows :

(i) Weight of watch glasses+clip=W_1 grams.

(ii) Weight of watch glasses+clip+copper sulphate crystals $=W_2$ grams.

(iii) Weight of watch glasses+clip+anhydrous copper sulphate $=W_3$ grams.

$\therefore$ Weight of copper sulphate taken=(W_2-W_1) grams.

Weight of anhydrous copper sulphate=(W_3-W_1) grams.

Weight of water of crystallisation$=(W_2-W_1)-(W_3-W_1)$
$=(W_2-W_3)$ grams.

Therefore, (W_2-W_1) grams of copper sulphate contain (W_2-W_3) grams of water of crystallisation.

$\therefore$ 100 grams of copper sulphate contain $\frac{(W_2 - W_3)}{(W_2 - W_1)} \times 100$ grams

$$\text{Percentage of water of crystallisation} = \frac{(W_2 - W_3)}{(W_2 - W_1)} \times 100$$

$= 36 \cdot 07$ (which is found by an actual experiment)

Deduction of the formula of blue vitriol. Let the formula of blue vitriol be $CuSO_4, nH_2O$. The value of n can be determined as follows :

$$\frac{\text{Weight of anhydrous copper sulphate}}{\text{Weight of water of crystallisation}} = \frac{1 \times \text{molecular weight of copper sulphate}}{n \times \text{molecular weight of water}}$$

$$\therefore \frac{(W_3 - W_1)}{(W_2 - W_3)} = \frac{1 \times 159 \cdot 5}{n \times 18} \quad [\because \text{ molecular weight of copper sulphate} = 159 \cdot 5\ ]$$

$$\therefore \frac{100 - 36 \cdot 07}{36 \cdot 07} = \frac{159 \cdot 5}{18n}$$

$\therefore$ n=5. Therefore, the formula of blue vitriol is $CuSO_4, 5H_2O$.

To prove that the water in the crystal exerts a definite vapour pressure. Let us take two barometers as shown in fig. 10.9. Initially, the mercury levels in both the barometers stand at the same height. A crystal of hydrated salt such as washing soda, copper sulphate, etc., is passed into the vacuous space of one of the barometer tubes. It is found that the mercury of the barometer tube sinks, showing that the water in the crystal is exerting a definite vapour pressure. The vapour pressure increases as the temperature is raised. This can be proved by putting a hot-water jacket round the upper part of the barometer tube.

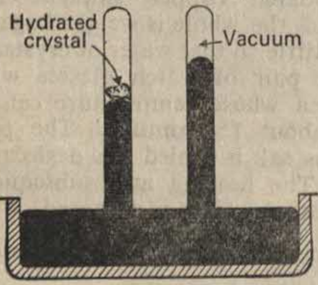


Fig. 10.9

Efflorescence. If a hydrated crystal is left exposed to the air, its stability depends on the pressure of the water vapour in the atmosphere. If the pressure of water vapour in the atmosphere is less than that of a hydrate, the hydrate will lose water of hydration to the atmosphere and form a lower hydrate or an anhydrous salt. The loss of water from a crystal of a hydrate is usually accompanied by the crumbling of the crystal to a powder. Such spontaneous loss of water of hydration is known as efflorescence.

Efflorescence is a phenomenon in which a hydrate spontaneously releases all or part of its water of crystallisation to the atmosphere.

Crystals of washing soda ($Na_2CO_3 \cdot 10H_2O$) when exposed to the atmosphere loses nine molecules of water of crystallisation to the air and falls to powder.

Deliquescence. If the pressure of the water vapour present in the atmosphere is greater than that of the crystal, water from the atmosphere enters into the crystal. This will continue until the vapour pressure of the crystal is the same as the pressure of the water vapour in the air. This phenomenon of absorbing water from the atmosphere by the crystals is known as deliquescence. In this process, the crystals ultimately turn into liquid.

Deliquescence is a phenomenon in which a crystal (or solid substance) absorbs water from the air to form a paste or eventually a solution.

Crystals of calcium chloride, magnesium chloride, etc., exhibit the phenomenon of deliquescence.

Some solids absorb moisture from the air without becoming damp or liquid. They are said to be hygroscopic. Examples are quicklime, anhydrous copper sulphate, etc. Some liquids such as concentrated sulphuric acid are also hygroscopic, i.e., they absorb moisture from the air.

COLLOIDS

Crystalloids and Colloids. In 1861, Thomas Graham found that certain substances such as salts, sugar, urea, etc., diffuse rapidly in solution and can pass through membranes such as parchment paper or collodion. These substances are crystalline in the solid state and were called by Graham *crystalloids*. On the other hand, there is a large group of substances such as glue, gelatin, albumin, starch, etc., which diffuse in solution very slowly and cannot pass through the membranes. These substances are amorphous in the solid state and were called *colloids* (from the Greek "Colla" : glue). Graham made a distinction between crystalloid and colloid as different kinds of substances. But, later investigations confirmed that this distinction between crystalloids and colloids is nevertheless very indefinite. For example, many typical colloids such as albumin can be obtained in the form of crystals and many indisputable crystalloids such as common salt can be obtained in the form of colloids. The same substance can behave like a colloid in some solvents and like a crystalloid in others. For instance, soap gives colloidal solutions in water but behaves as a crystalloid when dissolved in alcohol. Common salt can be brought into a colloidal state in benzene, but in water it is a typical crystalloid. Thus, it is more correct to speak only of the crystalloid or colloid state of substances just as we speak of their solid and liquid state. The colloid state, therefore, is characteristic of all substances when subjected to proper conditions.

Dispersions. When a fine powder of any insoluble substance such as clay is shaken with water, it is found that the larger particles settle at the bottom while the finest particles remain in water in a 'suspended' state for a considerable length of time but eventually all settle out. The solid can be separated completely from the mixture by filtration. If particles of a solid substance are suspended in a liquid, the system is called a *suspension.*

Any system in which the finely divided particles of one substance are distributed through another substance, is called a dispersed system ; the process of subdividing one substance into finely divided particles and scattering these through another substance is called dispersion. The divided substance is known as the dispersed phase, while the other substance is called the dispersion medium. For example, suspension of clay particles in water is the dispersion of clay particles in water ; the dispersed phase consists of clay particles while the dispersion medium is water. Thus, *suspension may be defined as the dispersion of the particles of a solid into a liquid.* Most suspensions are unstable and the dispersed phase eventually settles out completely.

Dispersed system may have different degrees of dispersion, depending on the size of the particles of the dispersed phase. Dispersed system in which the particles of the dispersed phase are coarse is known as coarsely dispersed system. Suspension falls into the category of coarsely dispersed system. On the other hand, true solutions are dispersed system in which the solutes (dispersed phase) are broken down into molecules and or ions and uniformly distributed throughout the solvent (dispersion medium). This is what happens when common salt is dissolved in water. Hence, solutions have very high or one may say, ultimate degrees of dispersion. An intermediate position is occupied by dispersed system in which the dispersed particles are intermediate in size between those in true solution and those in coarse suspension. Such systems are called colloidal solutions. Thus, the term *colloid* no longer refers to definite varieties of substance, but rather to particles of any kind whose dimensions lie within a certain range.

The sizes of the dispersed particles in dispersions of different degrees of fineness have been measured in various ways. On the basis of the sizes of the particles of the dispersed phase, a distinction among suspensions, colloidal solutions and true solutions can be made.

In suspensions, the particles have diameter larger than 10^{-4} cm, particles in true solution are usually smaller than 10^{-7} cm, the average diameter of the particles in colloidal solution lies in the range 10^{-7} cm to 10^{-4} cm.

Colloidal solution is defined as a dispersed system in which the size of the dispersed particles is larger than in true solution but less *than in coarse suspension; the sizes of the particles usually lie in the range 10^{-7} cm to 10^{-4} cm.* The dispersed particles do not settle no matter how long the colloidal solutions may stand and can pass through the filter papers, but can be detained by membranes of parchment paper, or bull bladder.

Solids colloidally dispersed in a liquid are referred to as *suspensoids*. The liquids which are dispersed colloidally into another liquid are known as emulsoids. The colloidal dispersion of a solid into a liquid is known as *sol*. A *sol* whose dispersion medium is water is known as *hydrosol*; when the dispersion medium is alcohol, the sol is known as *alcosol*, when the dispersion medium is benzene, the sol is called the *benzosol* and so on.

Dialysis. Colloidal particles can pass through the pores of ordinary filter paper but cannot pass through the pores of the membranes such as parchment paper, cellophane paper, animal membranes, etc. On the other hand, the particles of the dissolved substances in true solution can pass through the pores of the membrane. This property is utilised in separating the particles of dissolved substances from the colloidal particles. *The process of separating the colloidal particles from the particles of dissolved substances by membranes is known as dialysis.* The process is slow since the movement of particles through membrane is solely by diffusion.

The process of separating colloidal particles from those in true solution by means of diffusion through a membrane is called dialysis.

The apparatus used for dialysis is called a dialyser. The mixture of a colloidal substance and a substance in the dissolved state such as a solution of potassium iodide and starch is placed in a bag of parchment paper. The bag is then placed in distilled water(fig. 10.10). Potassium iodide diffuses freely through the membrane into the outer vessel but starch cannot penetrate the membrane and remains in solution in the bag. As a result, the bag will be found after some time to contain pure colloidal solution of starch.

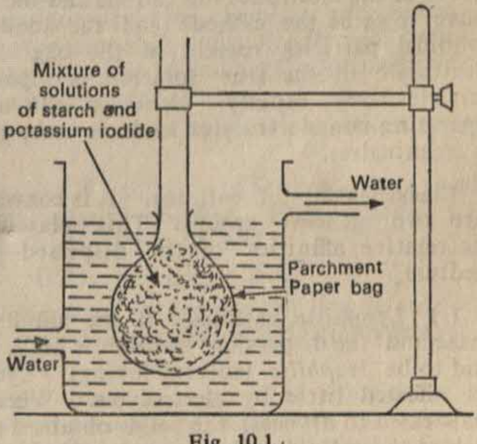


Fig. 10.1

If chlorine water is added to the water in the outer vessel, a yellow colouration is obtained due to liberated iodine. This shows that potassium iodide has passed through the membrane but the starch is retained, since if starch were present in the outer vessel, it would have given a blue colour with the iodine. Starch forms a blue coloured complex with iodine.

If in a mixture of colloidal solution and true solution the substance in the true solution is an electrolyte, then the electrolyte can be separated from the colloidal substance very rapidly by electro-dialysis. In this process, the mixture of the colloidal solution and true solution is taken in a bag and the bag is placed in water. Then two electrodes are placed into water in the outer vessel on the two sides of the bag. When electric current is passed by means of the electrodes the cations and the anions of the electrolyte move towards the cathode and the anode respectively while the colloidal particles remain in the bag. As a result, the dissolved electrolyte in the true solution is separated from the colloidal particles very rapidly. However, the use of electrodialyser for separating non-electrolytes such as urea, glucose, etc., from colloids is meaningless.

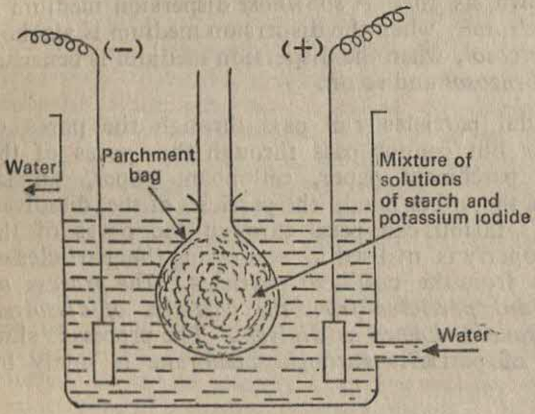


Fig. 10.11

Classification of colloids. It is convenient to classify colloids into two general groups. This classification is based upon the relative affinities of the dispersed phase for the dispersion medium.

(i) Lyophilic colloids. If the affinity between the dispersed phase and the dispersion medium is high, the colloidal substance is said to be *lyophilic* (solvent-loving). Lyophilic colloidal systems are affected little by electrolytes. When the lyophilic sols are evaporated to dryness, the solid obtained usually can be converted back to the colloidal dispersion merely by adding the liquid again. Such substances are also described as *reversible colloids*. The colloidal solution of starch in water is an example of a lyophilic sol. Other examples of lyophilic sols in water are glue, gums, gelatin, fats and soaps. Many lyophilic substances may become colloidally dispersed simply by contact with the dispersing liquid. For example, when soap comes in contact with water, it spontaneously disperses to form colloidal system. The dispersed phase in lyophilic colloidal solution is said to be *hydrophilic*, *alcophilic*, *benzophilic*, etc., when the dispersion medium is water, alcohol, benzene, etc., respectively.

(ii) **Lyophobic colloids.** If the affinities of the dispersed phase for the dispersion medium are small, the dispersed phase is said to be *lyophobic* (solvent-fearing or hating). When the lyophobic colloidal solutions are evaporated to dryness, the solid obtained cannot be brought back into the colloidal solution merely by adding water again. Lyophobic colloids, therefore, are also known as *irreversible colloids*. They are precipitated easily by the addition of electrolytes. Colloidal solution of silver chloride in water is an example of lyophobic colloids. Other examples are colloidal solutions of sulphur, metals, and metal sulphides in water. The dispersed phase in lyophobic colloidal solutions is said to be *hydrophobic*, *alcophobic*, etc., when the dispersion medium is water, alcohol, etc., respectively.

Preparation of colloidal solutions. The methods by which colloidal solutions are prepared are of two varieties, viz., dispersion method and condensation method. In dispersion method, larger particles are made smaller ones of colloidal dimensions, usually by grinding. Specially designed machines known as colloid mills are used for this purpose. In condensation method, the particles of molecular dimension combine to form aggregates of colloidal size. Such methods require chemical procedures. By adjusting the conditions, the insoluble substance formed during the reaction can, in many cases, be made to assume the form of colloidal particles, giving rise to a colloidal solution.

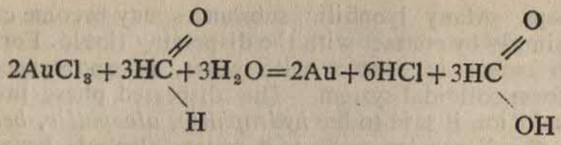
Some examples of the formation of colloidal solutions are given below :

(i) **Ferric hydroxide sol.** A solution of ferric chloride is added drop by drop into boiling water in a beaker. Ferric chloride undergoes hydrolysis and ferric hydroxide is formed :

$$FeCl_3 + 3H_2O = Fe(OH)_3 + 3HCl$$

Under these conditions, ferric hydroxide remains in solution as colloidal particles forming colloidal solution of ferric hydroxide. It is then purified by dialysis.

(ii) **Gold sol.** Several drops of 1 per cent solution of auric chloride, $AuCl_3$, are added to distilled water in a test tube. The solution is heated to boiling and then 2 or 3 ml. of a very weak solution of formalin are added to it. The liquid turns a beautiful purple colour due to the formation of colloidal particles of gold.



$$2AuCl_3 + 3HCHO + 3H_2O = 2Au + 6HCl + 3HCOOH$$

(iii) Arsenic trisulphide sol. When hydrogen sulphide is passed for some time through a solution of arsenic trioxide, a transparent golden-yellow sol of arsenic trisulphide is obtained.

$$As_2O_3 + 3H_2S = As_2S_3 + 3H_2O$$

(iv) Colloidal metals. Bredig's method. This method is used for the preparation of colloidal metals. For example, colloidal solution of silver is prepared as follows : Two silver wires are dipped into distilled water taken into a beaker. They are connected to a sufficiently powerful source of electric current and their ends are then brought together under the water. An electric arc is struck ; silver is vaporised by the arc and its vapour is then condensed by the surrounding liquid into particles of colloidal size. The entire liquid then turns brown due to the formation of colloidal solution of silver.

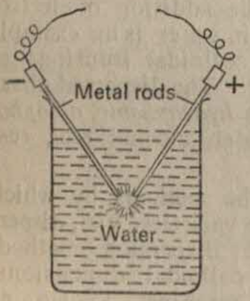


Fig. 10.12

Properties of colloidal solution.

(a) Optical properties. (i) Tyndall effect. When a beam of light is allowed to pass through a dark room, the dust particles floating in air become visible as tiny spots of light. When a beam of light is passed through a true solution, the path of the beam is not visible, but when it is passed through a colloidal solution, the path of the beam become visible as a streak of light and the liquid appears luminously turbid. This appearance is due to the reflection of some of the

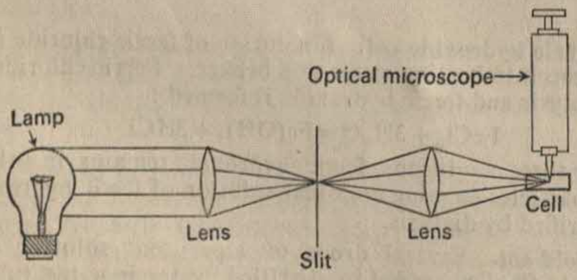


Fig. 10.13

incident light by the dispersed particles and is known as the *Tyndall effect.*

A strong converging beam of light is sent through a colloidal solution. When the path of the beam is viewed through a microscope whose axis is at the right angles to the direction of the beam, small flashes of light from the individual particles may be seen against the dark background. Such an arrangement of light source and the microscope is known as an *ultramicroscope.*

(b) **Brownian movement.** When observed by ultramicroscope, the colloidal particles are found to be in a state of rapid, irregular, dancing motion. Such irregular movement of colloidal particles is known as *Brownian movement* after the name of the English botanist Robert Brown, who first discovered it in 1827 in pollen grains suspended in water. The motion is caused by the irregular bombardment of the suspended colloidal particles by the molecules of the dispersion medium. The smaller the size of the colloidal particle, the more vigorous is its Brownian motion.

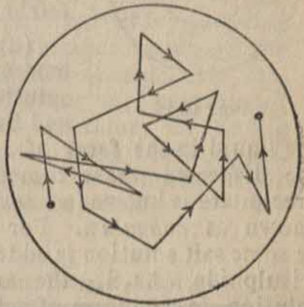


Fig. 10.14

(c) **Electrical properties.** (i) Electrophoresis. Nearly all colloidal particles are electrically charged, some positively and others negatively charged. When two electrodes connected to the poles of a current source of high voltage are dipped into a colloidal solution, the colloidal particles move slowly towards the anode or the cathode. This movement of colloidal particles in an electric field is known as *electrophoresis* (or as cataphoresis). Thus, when an electric current is passed through an As_2S_3 sol, the colloidal particles move towards the anode, proving that As_2S_3 particles bear a negative charge. On the other hand, when electric current is passed through ferric hydroxide sol, the particles move towards the cathode, indicating that they are positively charged.

All colloid particles in a given colloidal solution have the same type of charge. Sols of metallic hydroxides generally carry a positive charge whilst most other sols such as metals, As_2S_3, etc., carry a negative charge. An apparatus which is used for demonstration of electrophoresis is described below :

The apparatus consists of a U-tube which is half-filled with distilled water. About 5 grams of urea are added to about 50 c.c. of colloidal solution of arsenious sulphide to make the sol denser than water. The yellow colloidal solution is then run slowly by a pipet into the lower part of the U-tube. Platinum electrodes are placed in each arm of the U-tube. The electrodes are connected to the poles of a current source of sufficiently high voltage. After some time, the level of arsenious sulphide is found to fall on the cathode side of the U-tube and to rise on the anode side. This experiment, therefore, shows very clearly that arsenious sulphide moves towards the anode and hence the colloidal particles of arsenious sulphide sol are negatively charged.

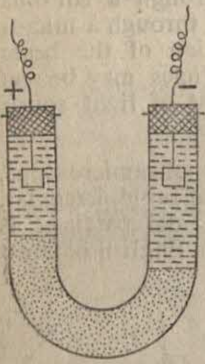


Fig. 10.15

The experiment may be repeated with the colloidal solution of ferric hydroxide which will be found to move towards the cathode. This proves that the particles of colloidal ferric hydroxide carry positive charges.

(d) **Coagulation of colloids.** If a small amount of an electrolyte is added to a colloidal solution, the solution first becomes turbid and finally the dispersed phase separates out of the liquid in the form of a precipitate. This process of separating the dispersed phase from the dispersion medium in the form of precipitate is known as *coagulation*; the solid which separates is known as *coagulum*. For example, when some hydrochloric acid or some salt solution is added to yellow colloidal solution of arsenic trisulphide, As_2S_3, the arsenic trisulphide separates out of the solution in the form of yellow precipitates.

The coagulation of a colloidal solution is due to neutralisation of the charge on the colloidal particles by the added electrolyte. When an electrolyte is added to a solution, it greatly increases the total concentration of ions in it. The colloidal particles adsorb ions of opposite sign. Thus, the initial charge of the colloidal particles are neutralised after which the coagulation of the sol occurs.

Emulsions. Emulsion is defined as a *stable colloidal system in which one liquid is dispersed into another liquid.* The common example of emulsion is milk in which fine particles of butter-fat is suspended in water.

If an oil such as kerosene is shaken with water, an emulsion of oil and water is obtained. Such emulsions are not stable and upon standing separation of the liquids into two layers occurs. If certain substances such as soap is added to the oil and water before shaking, the emulsion becomes stable. Such substances which stabilise the emulsions are known as *emulsifying agents* or *emulsifiers.*

Soaps and detergents are cleansing agents. The cleansing capacity of detergents and soaps depends upon their ability to act as emulsifying agents. Casein in milk acts as emulsifier.

The realm of colloids. Colloids are of greatest importance in our everyday life and industry. Every individual animal is built up from complex material called protoplasm which is colloidal. Hence, biological phenomena are connected with processes that take place in the colloidal dispersion of matter. Matter in the colloidal state also plays very important role in agriculture and in many industries such as tanning of leather, in the production of rayon, in the dyeing of textile fibres, in the manufacture of paints, photographic plates, etc Many of our foods are colloids. For example, milk is an emulsion of butter-fat in water. In ice cream, casein is present in colloidal state and is prevented from coagulating by the addition of protective colloids like albumin (white of egg) and gelatin. Many pharmaceutical preparations are either colloidal suspensions or emulsions. For example, colloidal gold is used for intermuscular injection, colloidal silver (argyol and protargol) is used in eye treatment. The blue colour of the sky is due to the scattering of blue light by the dust and water particles suspended in air. In soil, there exist various colloidal substances such as the humus, colloidal ferric hydroxide, aluminium hydroxide, clay, etc. Owing to the presence of these, soluble substances such as salts of potassium, phosphates and other substances necessary for the life of plant are retained in the soil instead of being washed away. Thus, it would not be exaggerative to say that the colloidal state of matter has been chosen by nature as the vehicle of life.

APPENDIX

Distinction between colloidal solution and true solution.

True solution	Colloidal solution
(1) In true solution, the average diameter of the dispersed particles is smaller than 10^{-7} cm.	In colloidal solution, the average diameter of the dispersed particles lies in the range 10^{-7} to 10^{-4} cm.
(2) True solutions can pass through the pores of the filter paper and the membranes of parchment paper, bull bladder, etc	Colloidal solutions can pass through filter paper but can be detained by membranes of parchment paper, bull bladder, etc.
(3) True solutions are homogeneous.	Colloidal solutions are heterogeneous.
(4) True solutions do not exhibit Brownian movement and Tyndall effect.	Brownian movement and Tyndall effect are characteristic of colloidal solutions only.
(5) True solutions cannot be coagulated.	Colloidal solutions can be coagulated.
(6) The colour of the true solution depends on the ions or molecules present in it.	The colour of the colloidal solution depends on the wavelength of light scattered by colloidal particles.

Problems

Ex. 1. 30 grams of water saturated with potassium nitrate at 80°C is cooled to 10°C. Calculate the weight of the salt deposited. Solubilities at 80 C and 10 C are 169 and 20·9 respectively.

100 grams of water are saturated with 169 grams of KNO_3 at 80°C.

∴ 30 grams of water are saturated with $\frac{169 \times 30}{100} = 50{\cdot}7$ grams of KNO_3 at 80°C. Similarly, 30 grams of water are saturated with $\frac{20{\cdot}9 \times 30}{100} = 6{\cdot}27$ grams of KNO_3 at 10°C.

∴ Weight of potassium nitrate deposited $= (50{\cdot}70 - 6{\cdot}27) = 44{\cdot}43$ grams.

Ex. 2. 30 c.c. of a sturated solution contain 22 grams of the solute at 30°C. If the specific gravity of the solution is 1·4, calculate the solubility of the substance at 30 C.

The weight of 30 c.c. solution $= 30 \times 1{\cdot}4 = 42$ grams.

∴ Weight of water $= 42 - 22 = 20$ grams.

∴ 20 grams of water contain 22 grams of the substance.

∴ 100 grams of water contain $\frac{22 \times 100}{20} = 110$ grams of the substance.

∴ The solubility of the substance at 30°C = 110.

Ex. 3. A hydrated sulphate of a bivalent metal contains 36·06% water of crystallisation. If the atomic weight of the metal is 63·5, calculate the number of molecules of water of crystallisation.

The formula of hydrated sulphate is MSO_4, nH_2O.

∴ Molecular weight of hydrated sulphate

$= 63{\cdot}5 + 32 + 4 \times 16 + n \times 18$

$= 159{\cdot}5 + n \times 18$

Now, $(159{\cdot}5 + n \times 18)$ grams of the hydrated salt contain $n \times 18$ grams of water.

∴ 100 grams of the salt contain $\frac{18n \times 100}{159{\cdot}5 + 18n}$ grams of water.

$$\therefore \quad \frac{18n \times 100}{159{\cdot}5 + 18n} = 36{\cdot}06$$

$$\therefore \quad n = 5$$

Hence, the number of molecules of water of crystallization is 5.

Ex. 4. 1 gram of a metal (at. wt. 27) is converted into 12·35 grams of a hydrated sulphate. If the hydrated sulphate contains

48·64% of water of crystallisation, what is the formula of the hydrated salt ?

100 grams of the hydrated salt contain 48·64 grams of water of crystallisation.

∴ 12·35 grams of the salt contain $\frac{48{\cdot}64\times12{\cdot}35}{100}=6{\cdot}007$ grams of water of crystallisation.

∴ Amount of anhydrous salt $=12{\cdot}35-6{\cdot}007=6{\cdot}343$ grams.

∴ Amount of sulphate in the anhydrous salt
$=6{\cdot}343-1=5{\cdot}343$ grams.

Again, the equivalent weight of sulphate $=\frac{96}{2}=48$

∴ 5·343 grams of sulphate combine with 1 gram of the metal.

Hence, 48 grams of sulphate combine with $\frac{1\times48}{5{\cdot}343}=8{\cdot}98$ grams of the metal. ∴ Equivalent weight of the metal $=8{\cdot}98$

Hence, the valency of the metal $=\frac{27}{8{\cdot}98}=3$

[∵ valency is a whole number]
∴ The formula of the hydrated salt is $M_2(SO_4)_3$, nH_2O
Molecular weight of the hydrated salt
$=2\times27+3\times96+18n=342+18n$

Hence, $(342+18n)$ grams of the salt contain $18n$ grams of water of crystallisation.

∴ 100 grams of the salt contain $\frac{18n\times100}{342+18n}$ grams of water of crystallisation. ∴ $\frac{18n\times100}{342+18n}=48{\cdot}64$

∴ $n=18$ [∵ n must be a whole number]
∴ The formula of the salt is $M_2(SO_4)_3$, $18H_2O$

EXERCISES

1. What do you understand by the terms, solution and solubility ? Describe how you would prepare a saturated solution. How would you determine whether a solution was (a) unsaturated, (b) saturated and (c) supersaturated ?

2. Define and illustrate : (a) saturated solution, (b) supersaturated solution (c) solubility (d) solubility curve and (e) dialysis.
Explain how supersaturated solution is originated.

3. How does the solubility of a solid substance in a liquid vary with temperature ? Explain this variation.

4. How would you determine the solubility of sodium chloride at room temperature ? "The solubility of lead nitrate at 100°C is 140"—Explain.

5. What is solubility curve ? What informations are obtained from solubility curve ? With the help of the solubility curve explain clearly the phenomenon of supersaturation. Suggest an explanation for the single break in the solubility curve for hydrated sodium sulphate and the double break in the curve for hydrated calcium chloride.

6. Give an explanation for the dissolution of a solute in a solvent. Why does the solubility of anhydrous sodium sulphate decrease with temperature ?

7. Define, with examples, the crystal and crystallisation. What is mother-liquor ? What do you mean by fractional crystallisation ?

8. What do you mean by water of crystallisation ? Make an experimental arrangement to prove that water in a crystal exerts pressure.

9. Define (a) efflorescence and (b) deliquescence. "Some substances are efflorescent and some substances are deliquescent"—Explain.

10. Write notes on : (a) solubility curve, (b) colloid, (c) dialysis and (d) water of crystallisation.

11. What do you mean by efflorescence and deliquescence ? Give examples. How would you determine the water of crystallisation of alum ?

12. Show and explain the nature of the solubility curve of hydrated sodium carbonate.

13. What is the difference between a colloidal solution and a true solution ? What do you mean by dialysis ?

14. What is Tyndall effect ? What do you mean by Brownian motion ? How would you separate colloidal solution from true solution ?

15. "Colloids are not a particular class of substances but they are a particular state of matter"—Explain.

16. At 100°C, 58·5 grams of barium chloride saturate 100 grams of water. If the solution is cooled to 10°C, what amount of barium chloride will separate out ? The solubility of barium chloride at 10°C is 36. [Ans. 22·5 gram]

17. At 20°C, 11·4 grams of lead nitrate saturate 20 grams of water. What is the solubility of lead nitrate at 20°C ? [Ans. 57]

18. 60 grams of a substance are required to saturate 80 grams of water at 50°C. What amount of the solute will separate when the solution is cooled to 10°C ? The solubility of the substance at 10°C is 50. [Ans. 25 gram]

19. 300 grams of potassium nitrate solution saturated at 100°C is cooled to 10°C. What amount of the salt will crystallise out ? The solubilities of potassium nitrate at 10°C and 100°C are respectively 20 and 250.
[Ans. 164·8 gm.] [H. S., '82]

20. The solubility of a salt at 30°C is 50. What amount of the salt will be required to prepare 60 gram of saturated solution of the salt ? [Ans. 20 grams]

21. Using the following data of lead nitrate, draw the solubility curve of lead nitrate.

Temperature	0°C	10°C	20°C	30°C	40°C	50°C	60°C
Solubility	41	48	57	65·5	75	84·5	95

22. 60 grams of a solution saturated at 20°C, on being evaporated to dryness, give 10 grams of the solute. What is the solubility of the salt at that temperature ? [Ans. 20]

23. The crystal of calcium chloride is represented by the formula $CaCl_2, nH_2O$. 6·98 grams of calcium chloride, on being heated, reduced to a constant weight equal to 3·5 grams. Find the value of n. [Ans. 6]

24. The crystal of calcium chloride ($CaCl_2, nH_2O$) contain 49·33% water of crystallisation. Determine the formula of calcium chloride crystal. Ca = 40, Cl = 35·5. [Ans. $CaCl_2, 6H_2O$]

CHAPTER XI

ELECTROLYSIS AND ELECTROLYTIC DISSOCIATION

Conductors and non-conductors. Substances which conduct electric current are called *conductors*. *Non-conductors* are substances which do not conduct electric current. There are two classes of conductors—(a) Metallic or electronic conductors, and (b) Electrolytic conductors.

(a) **Metallic or electronic conductor.** When electric current is passed through a copper wire, the wire is heated, but is otherwise unchanged. When the current is cut off, it regains its original properties as soon as it is cooled to its original temperature. Copper does not undergo any chemical change. Substances which conduct electric current without undergoing any chemical change are termed metallic or electronic conductors. In metallic conductors, the conduction of current is due to loose electrons in the conductors. The loose electrons are pushed from one atom to the next by the battery or generator. As a result, there is a flow of stream of electrons or conduction of current. The metallic conductivity decreases with increase of temperature.

(b) **Electrolytic conductors or electrolytes.** On the other hand, when electric current passes through water acidified with a little sulphuric acid, it causes a chemical decomposition in it, since hydrogen is given off at one electrode and oxygen at the other and this decomposition continues as long as the current flows. Substances which conduct electric current in solution or in the fused state and simultaneously undergo chemical change are called *electrolytes*. Substances which do not conduct current in solution are called *non-electrolytes*.

Pure water is a very poor conductor of electric current. But, if only a small amount of salt is dissolved in water or any acid or base added to it, water becomes good conductor of electricity. Hence, acids, bases and salts are called *electrolytes*. On the other hand, if sugar is dissolved in water, the solution obtained is equally poor conductor. Hence, sugar is a non-electrolyte.

Electric current can pass through fused or molten salts such as AgCl, and NaCl and fused hydroxides such as NaOH and KOH, and decomposes them. Dry salts, on the other hand, are not conductors of electric current. In electrolytic conduction, the current is carried by ions. The electrolytic or ionic conductivity increases with increase in temperature.

Electrolysis. Electrolysis may be defined as the chemical process which takes place, when an electric current is passed through the solution of an electrolyte. The apparatus in which the electrolysis is accomplished is known as *electrolytic cell*. As an illustration of the process, the electrolysis of zinc chloride is shown in fig. 11.1.

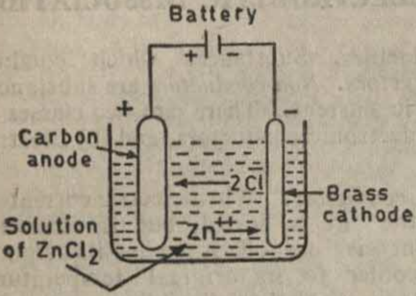


Fig. 11.1

A rectangular glass vessel is partly filled with the solution of zinc chloride in water. A strip of brass and a carbon rod are dipped into this solution as shown in fig. 11.1. The two rods are then connected to a storage battery or generator which supplies electricity. These rods which bring the current into and out of the solution are known as the electrodes. The electrode which is connected to the positive pole of the battery is called the positive electrode or anode and the electrode connected with the negative pole of the battery is called the negative electrode or cathode. Hence, the brass strip connected with the negative pole of the battery is the cathode and the carbon rod connected with the positive pole is the anode.

If we pass electric current through the solution by connecting the two electrodes of the battery, we see that grey metallic zinc is deposited on the brass cathode and that greenish yellow chlorine gas is liberated at the surface of the carbon electrode and escapes as gas bubbles. In this process, zinc chloride is said to be electrolysed and it undergoes chemical decomposition into metallic zinc and chlorine gas.

Theory of electrolytic dissociation. In order to explain the phenomenon of electrolysis, the Swedish scientist, Arrhenius, put forward the theory of electrolytic dissociation or ionisation. The subject-matter of his theory is as follows :

Fig. 11.2 : Arrhenius.

(i) When the electrolytes are dissolved in water, their molecules reversibly decompose or dissociate into ions. The ions formed remain in equilibrium with undissociated molecules. Each substance gives rise to two types of ions, positive ions and negative ions. The total number of positive charges acquired by positive ions must be equal to the total number of negative charges acquired by negative ions so that the solution as a whole remains electrically neutral. Thus, when sodium chloride is dissolved in water, it reversibly decomposes into positively charged sodium ion and negatively charged chloride ion :

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

the reversed arrow indicating that the ions may re-unite to form molecules of sodium chloride. Such reversible decomposition of the molecules of electrolytes into positive ions and negative ions, when they are dissolved in water. is called electrolytic dissociation. Further examples of electrolytic dissociation or ionisation are :

$$H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{--} \text{ ; } NaOH \rightleftharpoons Na^+ + OH^-$$

$$NH_4Cl \rightleftharpoons NH_4^+ + Cl^- \text{ ; } CuSO_4 \rightleftharpoons Cu^{++} + SO_4^{--}$$

(ii) *The degree of ionisation of an electrolyte is defined as the ratio of the number of ionised molecules to the total number of molecules dissolved*. That is, it is the fraction of the total electrolyte split into ions As the solution is diluted more and more, molecules are dissociated into ions and at infinite dilution, i.e., when the solution is extremely dilute. the dissociation of the electrolyte into ions becomes complete. This means that as the solution is diluted the equilibrium existing in solution between the unionised molecules and the ions shifts towards the formation of ions.

Electrolytes can be classed as *strong electrolyte* and *weak electrolyte* according to their ability of dissociating into ions. Electrolytes which dissociate feebly at moderate dilution, i e., which yield insignificant quantities of ions in aqueous solution are called *weak electrolytes.* Examples of weak electrolytes are weak acids such as acetic acid, carbonic acid, hydrocyanic acid, and weak bases such as ammonium hydroxide, etc. Electrolytes which readily dissociate into ions and show a very high degree of dissociation at moderate dilution are called *strong electrolytes.* Examples of strong electrolytes are strong acids such as hydrochloric acid, sulphuric acid, strong bases such as KOH, NaOH and salts like NaCl, KCl, $CuCl_2$, etc.

(iii) In the electrolytic conduction, the current is carried by ions. If a particular substance cannot dissociate into ions in solution, it will be a non-conductor of electric current.

(iv) The decomposition of the electrolyte into ions is not effected by the current but occurs as soon as the electrolyte is dissolved into water. The only effect of the current on the solution is that it makes the ions travel towards the electrodes. During the passage of a current in solution, the two ions travel in opposite directions ; the positive ions move towards the negative electrode or cathode and the negative ions move in opposite direction towards the positive electrode or anode. The positive ions which are attracted to the cathode are called *cations* and the negative ions which are attracted to the anode are called *anions*. When the ions reach the electrodes, they are discharged and simultaneously lose their charges and become neutral atoms or group of atoms which are deposited or liberated at the electrodes.

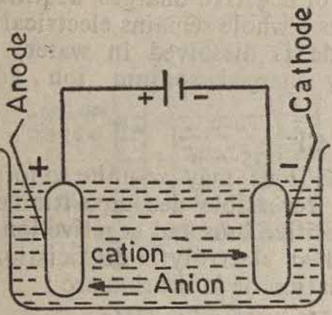


Fig. 11.3

The criticism of ionic theory and the mechanism of ionisation. The Arrhenius theory of electrolytic dissociation made no allowance for all the complexity of the phenomena taking place in solutions. For example, it regarded ions as absolutely free particles which are independent of the molecules of solvent. That is, it did not take account of any interaction of the particles of solute with those of solvents. It did not explain how could a mere solution in water serve to separate the different parts of the molecule (e.g., sodium ion and chloride ion in sodium chloride) since the attractive forces between them is very great. All these phenomena became clear when the structures of atoms and molecules were understood clearly.

It is now known that crystals of many electrolytes are built up not of molecules, but of positively and negatively charged ions arranged in a definite order in the crystal lattice and held in position by forces of electrostatic attraction. Therefore, when such electrolytes are dissolved in water, the ions pass into solution as independent units and not in the form of neutral molecules. which do not exist in the solid electrolyte. When a crystal of sodium chloride is brought in contact with water, the ions at its surface begin to attract the polar water molecules. The water molecules are attracted to the sodium ions by their negative poles and to the chloride ions by their positive poles. The molecules of water then orient themselves around the sodium and chloride ions as shown in fig. 10.3

But the water dipoles attract the ions with the same force as the ions attract the dipoles. Consequently, the attractive forces between the ions is weakened so greatly that the energy of the motions of molecules in the solution is enough to separate the ions from each other. The extent of attraction between the dipoles and the ions depends upon such factors as the radius of the ion, charge on the ion, and the dipole.

Many polar substances which consist of molecules (but not of ions) also decompose into ions when dissolved into water or other polar solvents. The mechanism of dissociation of polar molecules into ions is shown in fig. 11.4. The positive poles of water molecules attract the negative poles of the molecules of the electrolyte while the negative poles of water molecules attract the positive poles of the molecules of the electrolyte. Consequently, the polar molecule of the electrolyte is stretched by water molecules, moving its poles apart. As a result of this, the polar molecule of the electrolyte is broken down into separate ions. For example, when hydrogen chloride is brought in contact with water, the positive pole of hydrogen chloride is attracted by the negative poles of water molecules while the negative pole of hydrogen chloride is attracted by the positive poles of water molecules. As a result, the polar HCl molecule is stretched and broken down into separate ions, H^+ and Cl^-.

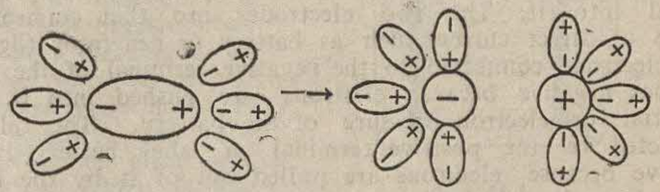


Fig. 11.4 : Change of polar structure to ionic structure.

After passing into solution, the ions may remain attached to water molecules. The ions combined with water molecules are called *ionic hydrates*. For example, each hydrogen ion, H^+ combines with a water molecule to form *hydronium* or *oxonium ion*, H_3O^+. Similarly, many cations such as Mg^{++}, Al^{+++}, etc., combine with water molecules to form their ionic hydrates such as $[Mg(H_2O)_6]^{++}$, $[Al(H_2O)_6]^{+++}$, etc. Anions such as Cl^-, Br^-, etc., are also hydrated or solvated. Obviously, therefore, the dissociation of the electrolyte does not result in the formation of ions but of compounds between ions and the solvent molecules (when the solvent is water, ionic hydrates are formed). The ionic hydrates formed are in a state of incessant disorderly motion and collide with one another. As a result of collisions they may combine to form hydrated molecules which may again be broken into the hydrated ions. Now, the more is the concentration of the solution, the greater is the number of collisions among the hydrated ions. Therefore, one may conceive that concentrated solutions contain hydrated ions in equilibrium with unionised molecules. In writing the ionisation equations, the formulas of the ions are written for the sake of simplicity instead of writing the formulas of the ionic hydrates. This is justified because the number of water molecules attached to the ion is not very often known and may vary with the concentration of the solutions and the temperature.

The mechanism of electrolytic conduction. Let an aqueous solution of a hypothetical electrolyte, M^+X^- be placed in a rectangular glass vessel. Two chemically inert electrodes are dipped into it. The two electrodes are then connected to a source of direct current such as battery or generator (fig. 11.5). The electrode connected to the negative terminal of the battery becomes negative because electrons are pushed into it by the potential or electron pressure of the battery. The electrode connected to the positive terminal of the battery becomes positive because electrons are pulled out of it by the battery. The electrode which becomes negative is called *cathode* (at this electrode, reduction takes place, i.e., electrons are gained), and the electrode, which becomes positive is called *anode* (at this electrode, oxidation takes place, i.e., electrons are removed). Thus battery or generator acts as an electron pump ; it pushes electrons into the cathode and pulls them out of the anode. Because electrons cannot move alone through the solution of the electrolyte, the battery cannot keep up the flow of electrons unless they are removed from the cathode and given up to the anode by the ions.

The molten electrolyte or the solution of the electrolyte, M^+X^-, contains equal numbers of positive ions, M^+ and negative ions, X^-. Attracted by the field of the negative electrode (cathode), positive ions, M^+, migrate to it where they gain electrons (and hence are reduced) and are converted into neutral atoms of M :

At cathode : $M^+ + e \rightarrow M$

Simultaneously, the negative ions, X^-, being attracted by the field of the positive electrode (anode), migrate to the positive electrode where they lose electrons (and hence are oxidised) and are converted into neutral atoms of X :

At anode : $X^- \rightarrow X + e$

Thus, if there is a loss of one electron at the anode (the anode gains it), there is a corresponding gain of one electron from the cathode (cathode loses it). Therefore, if two X^- ions give two electrons to the anode, there is effectively a flow of two electrons in the external circuit, from the anode of the electrolytic cell to the cathode of the voltaic cell at which they are gained. Two electrons are simultaneously liberated at the anode of the voltaic cell and they flow in the external circuit from the anode of the voltaic cell to the cathode of the electrolytic cell ; at the cathode, two

M^+ ions gain two electrons. Thus the number of electrons lost in the oxidation process $(X^- \rightarrow X + e)$ is equal to the number of electrons gained in the reduction process $(M^+ + e \rightarrow M)$, i.e., there exists a "conservation of electrons." With ions of unequal charge such as M^{+3} and X^- (for example, when the electrolyte is $AlCl_3$) the numbers of positive and negative ions which are discharged at the electrodes so adjust themselves as to maintain this equality. In the case of the electrolyte $M^{+3}(X^{-1})_3$, three anions, X^-, are discharged at the anode for each cation discharged at the cathode so that the number of electrons gained by the cation, M^{+3}, becomes equal to the number of electrons lost by the anion X^-.

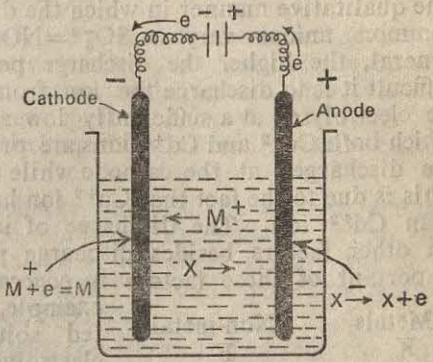


Fig. 11.5

The flow of current in the complete electric circuit as shown in fig. 11.5 is due to the movement of electrons in the external circuit and the migration of ions in both directions. The whole process of electric conduction in this system thus takes place in the following steps :

(i) Battery or generator or other source of direct current pushes electrons into the cathode.

(ii) Cations or positively charged ions move towards the negatively charged cathode. Cations combine with electrons from the cathode to form neutral atoms.

(iii) Anions or negatively charged ions move towards the anode and give up electrons to the anode and are converted into neutral atoms.

(iv) Electrons then flow in the external circuit from the anode through the source of potential to the cathode.

Discharge potentials. Different energies are required to discharge different ions from their aqueous solutions. For example, energy required to discharge the hydroxyl ions, OH^-, is smaller than the corresponding energy required to discharge the sulphate ions, SO_4^{--}. In general, the energies required to discharge an ion from aqueous solution are expressed in terms of *discharge potentials. Discharge potential may be defined as the minimum potential which must be impressed on an eletrode to discharge an ion from its normal solution.* The discharge potentials of some common metallic ions vary in the order

$$Na^{+1} > Zn^{+2} > Fe^{+2} > Cd^{+2} > Sn^{+2} > Pb^{+2} > Cu^{+2} > Ag^{+1}.$$

The qualitative manner in which the discharge potentials for some common anions vary is $SO_4^{-2} = NO_3^{-1} > OH^- > Cl^- > Br^- > I^-$. In general, the higher the discharge potential of an ion, the more difficult it is to discharge the ion from solution. For example, if we electrolyse, at a sufficiently low applied potential, a solution at which both Cu^{+2} and Cd^{+2} ions are present, then only Cu^{+2} ions are discharged at the cathode while Cd^{+2} ions remain in solution. This is due to the fact that Cu^{+2} ion has lower discharge potential than Cd^{+2} ion. The discharge of ion from solution also depends on other factors besides discharge potential. One of the most important of these factors is *concentration of the solution.* For example, when moderately concentrated solution of Cu(II) chloride is electrolysed, copper and chlorine are obtained while the electrolysis of dilute solution of Cu(II) chloride yields copper and oxygen. Thus, whether chlorine or oxygen is obtained depends on their relative concentration in solution. Another factor on which discharge of ions depends is the *material of the electrode* at which they are discharged. For example, when sodium chloride solution is electrolysed using an inert electrode such as gas-carbon electrode or platinum electrode, H^+ ions are discharged at the cathode while on electrolysis of sodium chloride solution using mercury cathode, Na^+ ions are discharged at the cathode.

Metals	Non-metals
K	F
Na	O
Ba	Cl
Sr	Br
Ca	I
Mg	S
Al	P
Cr	N
Mn	B
Zn	
Cd	C
Fe	Si
Co	
Ni	
Sn	
Pb	
H	
Sb	
Bi	
As	
Cu	
Hg	
Ag	
Pt	
Au	

Fig. 11.6 : Electrochemical series.

From the foregoing discussions, we can derive the following conclusions :

(i) At the cathode, positively charged ions gain electrons (and are discharged, e.g., $M^+ + e \rightarrow M$).

(ii) At the anode, negatively charged ions lose electrons (and are discharged, e.g., $X^- \rightarrow X + e$).

(iii) The more easily a metal yields electrons, the less readily its ions are discharged. Thus other conditions being equal, the ions of the metals at the top of the electrochemical series (fig. 11.6) are discharged least readily while ions of the metals at the bottom of the electrochemical series are discharged most readily. For example, other conditions being equal, gold ion, Au^+, is discharged much more readily than zinc ion, Zn^{++}.

(iv) The more easily a non-metal accepts electrons (or the less readily the anions give up their charges), the less readily its ions (anions) are discharged. Thus, other conditions remaining the same, iodide ion, I^-, is discharged more readily than bromide ion, Br^-, and bromide ion is discharged more readily than chloride ion.

(v) The higher the discharge potential of an ion, the more difficult it is to discharge the ion from the solution. The lower the discharge potential of an ion, the more readily the ion is discharged. Thus hydroxyl ions, OH^-, are discharged more readily than sulphate, SO_4^{-2} or nitrate, NO_3^- ions.

(vi) The higher is the discharge potential of an ion, the higher is the energy required to discharge the ion, i.e., higher potential (from an external source) must be impressed on the electrode to discharge the ion from the solution. For example, from a solution of $CuCl_2$ and $ZnCl_2$, only Cu^{++} ions are discharged at a voltage, say of 1·2 volts but not zinc ions Zn^{++} ions are discharged at a voltage much higher than 1·2 volts. In general, the ions of the metals at the top of the electro-chemical series are discharged at higher applied potential while the ions of the metals at the bottom of the electro-chemical series are discharged at lower applied potential.

The foregoing points must be borne in mind while considering the examples of electrolysis.

Explanation of the phenomenon of electrolysis in the light of the theory of electrolytic dissociation. (i) Electrolysis of molten sodium chloride, NaCl. Molten sodium chloride is taken into a crucible and two carbon electrodes are dipped into it. An electric potential from a battery or generator is applied when sodium is deposited at the cathode and chlorine gas is liberated at the anode. The process can be explained as follows: solid sodium chloride consists of equal number of sodium ions and chloride ions. If sodium chloride is molten, the ions are free to move. Electrons are pushed into the cathode by the potential of the direct current source and hence the cathode becomes negative. Simultaneously, electrons are removed from the anode and hence the anode becomes positive. Attracted by the field of negative electrode, Na^+ ions migrate to it where they gain electrons (and hence are reduced) and are converted into neutral sodium atoms :

At cathode : $Na^+ + e \rightarrow Na$ (11·1)

Simultaneously, chloride ions, Cl^-, move at the anode and give up electrons to the anode (and hence are oxidised) to become chlorine atoms. Since chlorine atoms cannot exist independently, two chlorine atoms combine to form a stable Cl_2 molecule. So the oxidation of Cl^- ion is written directly as :

At anode : $2Cl^- \rightarrow Cl_2 + 2e$ (11.2)

The over-all reaction for the electrolytic decomposition is the sum of the two electrode reactions (11·1) and (11·2). Since two electrons are given at the anode by the two Cl^- ions, two Na^+ ions must simultaneously gain two electrons from the cathode for the *conservation of electrons*. Hence, the net result of electrolysis is

$$\begin{array}{rll} \text{At cathode :} & 2Na^+ + 2e & = 2Na \\ \text{At anode :} & 2Cl^- & = Cl_2 + 2e \\ \hline \text{Electrolytic cell :} & 2Na^+ + 2Cl^- & = 2Na + Cl_2 \end{array}$$

The charge of the electrons is, therefore, conducted by the motions of the sodium ions and the chloride ions. Thus the continuation of the electron stream through the wire is made possible by the decomposition of sodium chloride into sodium ions and chloride ions. Thus the whole process of the electric conduction in molten sodium chloride takes place in the following steps :

(i) Generator or battery pushes electrons into the cathode.

(ii) Na^+ ions migrate to the cathode and take up electrons carried by it to become neutral sodium atoms.

(iii) Cl^- ions migrate to the anode and give up electrons to become Cl atoms. Two chlorine atoms then combine to form a molecule of chlorine.

(iv) Electrons then move from the anode through the battery or generator to the cathode.

(ii) Electrolysis of aqueous solution of sodium chloride. Let us take *moderately concentrated aqueous solution* of sodium chloride in a rectangular glass vessel and two platinum electrodes are dipped into it. The electrodes are connected to a source of direct current such as battery. On electrolysis of this solution (moderately concentrated aqueous solution of NaCl) hydrogen is liberated at the cathode and chlorine gas at the anode, while OH^- ion is produced in the solution. We can account for these products in the following way :

In molten NaCl, only two ions, viz., Na^+ and Cl^-, are present in the electrolyte. Hence, only one reaction is possible at each electrode—the discharge of Na^+ ions (i.e., reduction of Na^+ ion) at the cathode to form neutral sodium atom and the discharge of Cl^- ion (i.e., oxidation of Cl^- ion) at the anode to form neutral chlorine atom. But in aqueous solution of sodium chloride, there are Na^+, Cl^-, H^+ and OH^- ions. Na^+ and Cl^- ions are formed by the dissociation of NaCl :

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

and H^+ and OH^- ions are formed by the ionisation of water :

$$H_2O \rightleftharpoons H^+ + OH^-$$

Hence, in the solution, there are more than one species of cations, viz., Na^+ and H^+. We see that sodium is higher than hydrogen in the electrochemical series. Hence, sodium atom has higher tendency to form Na^+ ion than does hydrogen atom to form H^+ ion. Conversely, H^+ ion more readily accepts electron than does Na^+ ion. Also discharge potential of H^+ ion is less than that of Na^+ ion. Hence, H^+ ion is more readily reduced to the elemental state than is Na^+ ion. Therefore, H^+ ions are discharged at the cathode and yield atoms of hydrogen ; the atoms of hydrogen unite to form hydrogen molecules which escape as gas. In the electrolysis of aqueous NaCl solution, therefore, no Na^+ ion is discharged at the cathode.

$$\text{At cathode : } 2H^+ + 2e = H_2 \qquad (11{\cdot}3)$$

As H^+ ions are discharged at the cathode, water molecules ionise to maintain the H^+ ion concentration :

$$2H_2O \rightleftharpoons 2H^+ + 2OH^- \qquad (11{\cdot}4)$$

Hence, the net cathode reaction is obtained by adding (11·3) and (11·4).

$$\begin{array}{rcl} 2H^+ + 2e & = & H_2 \\ 2H_2O & = & 2H^+ + 2OH^- \\ \hline \text{At cathode : } 2H_2O + 2e & = & H_2 + 2OH^- \end{array}$$

Hence, the discharge of H^+ ions leaves in solution an excess of OH^- ions. These, with Na^+ ions, which remain unaffected by electrolysis constitute a solution of sodium hydroxide, NaOH.

In the solution two anions, viz., Cl^- and OH^- are present. The discharge potential of Cl^- ion is less than that of OH^- ion. Hence, at anode Cl^- ion is discharged.

$$\text{At anode : } 2Cl^- = Cl_2 + 2e$$

This conclusion is further supported by the fact that Cl^- ion is less electronegative than OH^- ion. Hence Cl^- ions are oxidised to Cl_2 ; OH^- ions do not undergo anodic oxidation.

Thus the net reaction for the electrolysis of an aqueous solution of NaCl are

$$\begin{array}{lrcl} \text{At cathode : } & 2H_2O + 2e & = & H_2 + 2OH^- \\ \text{At anode : } & 2Cl^- & = & Cl_2 + 2e \\ \hline \text{Electrolytic cell : } & 2H_2O + 2Cl^- & = & H_2 + Cl_2 + 2OH^- \end{array}$$

Hence, the products of electrolysis of moderately concentrated solution of NaCl are H_2, Cl_2 and NaOH.

Electrolysis of *dilute solution of sodium chloride* produces hydrogen at the cathode and oxygen at the anode. In the solution, two cations, viz., Na^+ and H^+ are present. Of these two cations, H^+ ion is discharged at the cathode. Hence, at cathode, hydrogen is evolved.

At cathode : $4H^+ + 4e = 2H_2$ (11·5)

As the H^+ ion is reduced at the cathode, water molecules ionise to maintain the H^+ ion concentration : $H_2O \rightleftharpoons H^+ + OH^-$.

The two anions, viz., Cl^- and OH^- are present in the solution. Both migrate to the anode. Since the concentration of OH^- ion is much greater than Cl^- ion, the OH^- ion is discharged at the anode :

$$\begin{aligned} \text{At anode : } 4OH^- &= 4OH + 4e \\ 4OH &= O_2 + 2H_2O \\ \hline \text{At anode : } 4OH^- &= O_2 + 2H_2O + 4e \qquad (11\cdot6) \end{aligned}$$

Thus oxygen is liberated at the anode. The over-all reaction occurring in the cell is described by adding (11·5) and (11·6).

$$\begin{aligned} \text{At cathode : } 4H^+ + 4e &= 2H_2 \\ \text{At anode : } 4OH^- &= O_2 + 2H_2O + 4e \\ \hline \text{Electrolytic cell : } 4H^+ + 4OH^- &= 2H_2 + O_2 + 2H_2O \\ \text{or, } 4H_2O &= 2H_2 + O_2 + 2H_2O \end{aligned}$$

The electrolysis of dilute aqueous solution of other electrolytes such as sodium sulphate, potassium chloride, sodium hydroxide, potassium hydroxide, etc., is closely similar to that of dilute aqueous solution of sodium chloride, producing hydrogen at the cathode and oxygen at the anode. Electrolysis of fused sodium hydroxide yields sodium at the cathode and oxygen at the anode.

(iii) **Electrolysis of sodium chloride solution using a mercury cathode.** If moderately concentrated solution of sodium chloride is electrolysed using mercury cathode and graphite anode, Na^+ ion is discharged at the cathode and chlorine is evolved at the anode. During electrolysis, both Na^+ ion and H^+ ion migrate to the cathode. In mercury sodium dissolves (forming sodium amalgam) and consequently, its activity is greatly reduced. As a result, Na^+ ion is discharged at the mercury cathode and not H^+ ion :

At cathode : $Na^+ + e = Na$

In solution two anions, viz., Cl^- and OH^- are present. Both of them migrate to the anode. Since Cl^- ion has a lower discharge potential than OH^- ion, Cl^- ion is discharged at the anode and chlorine is evolved :

At anode : $2Cl^- = Cl_2 + 2e$

The net reaction, therefore, is :

$$\begin{array}{ll} \text{At cathode : } 2Na^+ + 2e & = 2Na \\ \text{At anode : } 2Cl^- & = Cl_2 + 2e \\ \hline \text{Electrolytic cell : } 2Na^+ + 2Cl^- & = 2Na + Cl_2. \end{array}$$

(c) **Electrolysis of water.** Water is a very weak electrolyte and consequently a very poor conductor of electricity. But when a little sulphuric acid is added to it, it becomes a good conductor and allows current to pass freely and only water is decomposed. An apparatus for the electrolysis of water is shown in fig. 11.7. It is called a voltameter (or better a coulometer). It consists of two glass tubes with stop-cocks connected by a horizontal tube. The horizontal tube is fitted with a funnel which acts as reservoir of water. The electrodes consist of pieces of platinum foil which are fitted with the two glass tubes as shown in the figure.

The two glass tubes are incompletely filled with acidulated water by pouring it through the funnel. By connecting the electrodes to the two poles of the battery, electric current is passed through water. Oxygen is liberated at the anode and hydrogen at the cathode.

Water acidified with sulphuric acid contains hydrogen ions, H^+, hydroxyl ions, OH^- and sulphate ions, SO_4^{--}. These ions are produced as a result of the following dissociations :

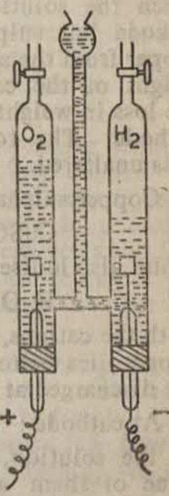


Fig. 11.7

$$H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{--}$$
$$2H_2O \rightleftharpoons 2H^+ + 2OH^-$$

During electrolysis, the positively charged hydrogen ions, H^+ move towards the cathode and are discharged there :

$$\text{At cathode : } 4H^+ + 4e = 2H_2 \qquad (11{\cdot}7)$$

Both negatively charged hydroxyl ion, OH^- and sulphate ion, SO_4^{--} move towards the anode. Since OH^- ion has lower discharge potential than sulphate ion, SO_4^{--}, hydroxyl ions are discharged at the anode :

$$\begin{array}{ll} \text{At anode : } 4OH^- & = 4OH + 4e \\ 4OH & = O_2 + 2H_2O \\ \hline \text{At anode : } 4OH^- & = O_2 + 2H_2O + 4e \end{array} \qquad (11{\cdot}8)$$

The over-all reaction occurring in the voltameter is described by adding the equations (11·7) and (11·8).

At cathode : $4H^+ + 4e = 2H_2$
At anode : $4OH^- = O_2+2H_2O+4e$

Electrolytic cell : $4H^+ + 4OH^- = O_2+2H_2O+2H_2$
or, $4H_2O = O_2+2H_2O+2H_2$

(d) **Electrolysis of copper sulphate solution.** (i) **Using copper electrodes.** A rectangular glass vessel is partly filled with copper sulphate solution. Two stout copper plates are used as electrodes. When the solution is electrolysed, copper is deposited on the cathode but sulphate ions are not discharged at the anode. Instead copper from the anode goes into the solution as Cu^{++}. Hence, the weight of the cathode increases while that of the anode decreases ; the loss in weight of anode is equal to the gain in weight of the cathode. The total amount of copper sulphate in the solution is thus unaltered.

Copper sulphate when dissolved into water dissociates as :

$$CuSO_4 \rightleftharpoons Cu^{++} + SO_4^{--}$$

Water also ionises into hydrogen ion, H^+, and hydroxyl ion, OH^- :

$$H_2O \rightleftharpoons H^+ + OH^-$$

Both the cations, Cu^{++} and H^+, move towards the cathode. Since copper lies below hydrogen in the electrochemical series, Cu^{++} ions are discharged at the cathode and not H^+ ions.

At cathode : $Cu^{++} + 2e = Cu$

In the solution, there are two anions, viz., SO_4^{--} and OH^-. But none of them are discharged at the copper anode because the abilities of these ions to lose electrons is less than that of the copper atoms composing the anode. The copper atoms of the anode, therefore, pass into solution as Cu^{++} ions ; in short, the anode dissolves. In doing this, the copper atom leaves two electrons in the anode ; these electrons then flow in the external circuit from the anode through the source of potential to the cathode.

Thus, during the electrolysis of copper sulphate solution, the total amount of $CuSO_4$, i.e., Cu^{++} SO_4^{--} remains the same before and after the electrolysis. Copper from the anode goes into the solution as Cu^{++} ions which are discharged and deposited at the cathode.

(ii) **Using platinum electrodes.** When platinum electrodes are used in the electrolysis of copper sulphate, copper is deposited at the cathode and oxygen is liberated at the anode. This observation may be explained as follows :

Copper sulphate in solution dissociates into cupric ions and sulphate ions : $CuSO_4 \rightleftharpoons Cu^{++} + SO_4^{--}$

Similarly, water dissociates as : $H_2O \rightleftharpoons H^+ + OH^-$. Under the action of electric current, both Cu^{++} and H^+ ions migrate towards the cathode. Of these two cations, only Cu^{++} ions are discharged at the cathode, since copper lies below hydrogen in the electrochemical series :

At cathode : $Cu^{++} + 2e = Cu$

Both SO_4^{--} ions and OH^- ions go to the anode. Since the discharge potential of OH^- ion is less than that of SO_4^{--} ion (OH^- ion is less electronegative than SO_4^{--} ion), OH^- ions are discharged at the anode with the evolution of oxygen :

At anode : $4OH^- = 2H_2O+O_2+4e$

The sulphate ions combine with H^+ ions produced from water and form sulphuric acid : $SO_4^{--} + 2H^+ \rightleftharpoons H_2SO_4$

The net effect is that Cu^{++} ions and OH^- ions are discharged, and H^+ and SO_4^{--} ions, i.e., sulphuric acid is produced. Thus, copper sulphate is removed from the solution and replaced with equivalent amount of sulphuric acid.

Electrical units. A direct current of electricity passing through a wire is a flow of electrons along the wire. The quantity of electricity is measured in coulombs. Thus the coulomb (symbol Q) is a measure of the quantity of electricity that flows in a circuit in a given interval of time. Therefore, a coulomb represents the flow of a definite number of electrons. 96,500 coulombs represent the flow of $6{\cdot}023 \times 10^{23}$ electrons, i.e., the Avogadro number of electrons.

The rate of flow of electricity is the quantity of electricity passing through a given point of the wire in unit time and is measured in *amperes* or *coulombs per second*. Hence, the *ampere* (symbol C) is a measure of the rate of flow of electrons. One ampere is a flow of current which is equal to one coulomb per second. Hence, we can write : $C=\frac{Q}{t}$ where C is the current in amperes, Q is the quantity of electricity in coulombs and t is the time in seconds.

$\therefore\ Q=C\times t$

i.e., coulomb=ampere × second

That is, if C ampere of current flows for t seconds the quantity of electricity in coulombs is given by

Q (in coulombs)$=C\times t$

Practical units. One ampere is the quantity of electricity which, when passed through a solution of a silver salt for one second deposit 0·001118 gram or 1·118 milligram of silver at the cathode.

One coulomb is the quantity of electricity carried by a current of one ampere in one second. Hence, one coulomb of electricity deposit 0·001118 gram of silver from a solution of a silver salt at the cathode.

The quantity of electricity which, when passed through a solution of an electrolyte deposit one gram-equivalent of a substance is called one Faraday of electricity.

Now, 0·001118 gram of silver is deposited by 1 coulomb of electricity. Hence, 107·88 grams of silver are deposited by $\frac{107{\cdot}88}{0{\cdot}001118}$ =96,500 coulombs of electricity.

Hence, one Faraday=96,500 coulombs.

Quantitative aspects of electrolysis. Faraday's laws. In 1832, Michael Faraday, an English Physicist, carried out the quantitative study of the phenomenon of electrolysis. As a result of his study, he established the relationship between the quantity of electricity flowing through a solution of an electrolyte and the amount of the electrolyte which is decomposed. These relationships can be stated in the form of two laws known as the Faraday's laws of electrolysis :

First law : *The weight of a substance deposited at an electrode by electrolysis is directly proportional to the quantity of electricity flowing through the solution.*

Let W grams of a substance be deposited at any electrode during electrolysis when Q coulombs of electricity flow through the solution. Then according to the first law of Faraday,

$$W \propto Q \quad \therefore \quad W \propto C \times t \quad \therefore \quad W = Z \times C \times t \qquad (11{\cdot}9)$$

where Z is a constant called the electrochemical equivalent.

Electrochemical equivalent (E. C. E.). If we put Q=1 coulomb (i.e., C=1 ampere and t=1 sec.), then the equation (11·9) becomes

$$W = Z$$

Hence, electrochemical equivalent, Z, is defined as the amount of the substance in grams deposited by the passage of 1 coulomb of electricity, i.e., by the passage of 1 ampere of current for 1 second. It has been found experimentally that 1 coulomb of electricity deposits 0·001118 gram of silven from the solution of silver nitrate. Hence, E. C. E. of silver is 0·001118 gram/coulomb or 1·118 mg/coulomb.

Again, when 1 coulomb of electricity is passed through hydrochloric acid solution 0·0000104 gram of hydrogen is liberated. Hence, the electrochemical equivalent of hydrogen is 0·0000104 gram/coulomb or 0·0104 milligram/coulomb. The electrochemical equivalents of some known elements are given in table 11.1.

Table 11.1

Element	Electrochemical equivalent (milligram/coulomb)	Element	Electrochemical equivalent (milligram/coulomb)
Hydrogen	0·01045	Iodine	1·3152
Oxygen	0·0829	Copper	0·3294
Chlorine	0·36743	Iron	0·2893
Silver	1·1180	Zinc	0·3388
Cadmium	0·5824	Magnesium	0·126
Bromine	0·8281		

Faraday's first law can be verified as follows: A current of definite ampere is passed through an electrolyte for different times and the amount of the substance deposited at the electrode is determined. When the amount of the substance is plotted against the quantity of electricity passed through the electrolyte, a straight line is obtained. This proves Faraday's first law.

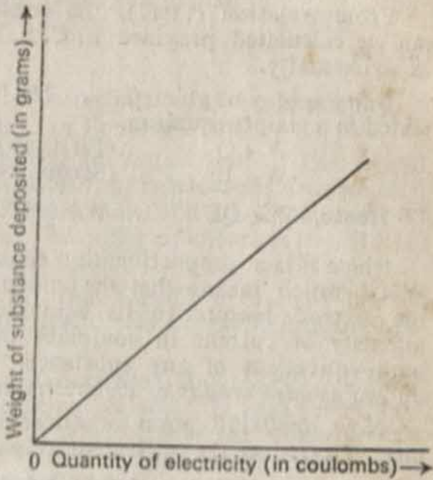


Fig. 11.8

Second law. *When the same quantity of electricity is passed through different electrolytes, the amounts of different substances deposited at the electrodes are proportional to their chemical equivalents.*

Let the same quantity of electricity (say Q coulombs) pass through the solutions of the two different electrolytes. Let W_1 grams of A whose equivalent weight is E_1 be deposited from the first electrolyte and W_2 grams of B whose equivalent weight is E_2 be deposited from the second electrolyte. Then by the second law,

$$\frac{W_1}{W_2}=\frac{E_1}{E_2} \qquad (11{\cdot}10)$$

But according to the first law, $W_1=Z_1Q=Z_1\times C\times t$ and $W_2=Z_2Q=Z_2\times C\times t$ where Z_1 and Z_2 are E. C. E. of A and B respectively. Hence, $\frac{W_1}{W_2}=\frac{Z_1}{Z_2}$ (11·11)

From (11·10) and (11·11) we get $\frac{Z_1}{Z_2}=\frac{E_1}{E_2}$

Thus, $\frac{\text{E. C. E. of A}}{\text{E. C. E. of B}}=\frac{\text{C. E. of A}}{\text{C. E. of B}}$

If A is any element and B is hydrogen, we have

$$\frac{\text{E. C. E. of any element}}{\text{E. C. E. of hydrogen}}=\frac{\text{C. E. of the element}}{\text{C. E. of hydrogen}}$$

or, $\frac{\text{E. C. E. of any element}}{\text{E. C. E. of hydrogen}}=$C. E. of the element (since equivalent weight of hydrogen is 1) or, E. C. E. of any element = C. E. of the element × E. C. E. of hydrogen = C. E. of the element × 0·0000104 (11·12)

From relation (11·12), the equivalent weight of an element can be calculated provided E. C. E. of the element is determined experimentally.

One Faraday of electricity. The two laws of Faraday can be stated in a simple equation.

$$W \propto Q \qquad \text{(First law)}$$
$$W \propto E \qquad \text{(Second law)}$$

$$\text{Hence, } W \propto QE \qquad \therefore \; W = \frac{1}{F} QE \qquad (11{\cdot}13)$$

where F is a proportionality constant. If we put $F=Q$, then $W=E$ which means that the amount of any substance deposited at the electrode is equal to its equivalent weight. Hence, F is the quantity of current in coulombs that is required to deposit one gram-equivalent of any substance. This quantity of current is known as *one Faraday of electricity* and is represented by F.

Now, 0·001118 gram of silver is deposited by 1 coulomb of electricity. Since the equivalent weight of silver is 107·88 ; one gram-equivalent of silver (i.e., 107·88 grams) are deposited by $\frac{1 \times 107{\cdot}88}{0{\cdot}001118}$ =96,494 coulombs which for most purposes may be rounded off to 96,500 coulombs.

Hence, one Faraday of electricity (F) equals 96,500 coulombs which liberate one gram-equivalent of any substance. That is, one Faraday of electricity will deposit 1·008 grams of hydrogen, 8·000 grams of oxygen, 22·991 grams of sodium, 35·45 grams of chlorine and 20·04 grams of calcium. On this basis, therefore, the second law is more precisely expressed in the form : *One Faraday of electricity or 96,500 coulombs will liberate one gram-equivalent of any substance from the solution of an electrolyte.*

The laws of Faraday are summarised in the following equation :

$W = \frac{1}{F} QE$ which may be written in three forms :

(i) $\frac{Q}{F} = \frac{W}{E}$

$$\text{or, } \frac{\text{Actual number of coulombs passing through solution}}{\text{96,500 coulombs}} = \frac{\text{Actual weight in grams of substance deposited}}{\text{one gram-equivalent weight}}$$

(ii) $\frac{C \times t}{F} = \frac{W}{\frac{A}{n}}$ where C=current in amperes

t=time in seconds

W=weight in grams of the element deposited.

A = atomic weight of the element

n = valency of the element in the compound.

(iii) $$W=\frac{C\times t}{F}\times\frac{A}{n} \qquad (11\cdot14)$$

It is thus seen that neither the voltage nor any concentration is directly concerned in the statement of Faraday's laws.

Faraday's laws are also applicable to voltaic cells. The weight of a substance which undergoes electrode reactions in a voltaic cell is also proportional to its equivalent weight and to the number of coulombs delivered by the voltaic cell. The equations (11·9), (11·10) and (11·11) are thus applicable.

Experimental verification of the Faraday's second law of electrolysis The following experiment may be performed in order to illustrate the second law.

Solutions of four different substances, viz., HCl, $AgNO_3$, $CuSO_4$ and $FeCl_3$ are taken in four different vessels. In each vessel, two platinum electrodes are dipped. The electrodes are connected in series so that the same quantity of electricity passes through each solution. The current is allowed to pass for some time so that sufficient quantity of electrolysis products accumulate on the electrodes. The current is then switched off and the substances deposited are weighed. It is found that if one gram of hydrogen is deposited during electrolysis, then 107·9 grams of silver, 31·8 grams of copper and 18·6 grams of iron are deposited from the respective solutions; the gram-equivalent weight of silver, copper and iron (in $FeCl_3$) being 107·9, 31·8 and 18·6 grams respectively. In other words, the weights of the substances deposited at the cathode equal their gram-equivalents Similarly, if the quantities of the substances deposited at the anodes are measured, it is found that in the vessel I and IV, 35·5 grams of chlorine are liberated at the anode and in the vessel II and III 8 grams of oxygen are liberated at the anode. Thus, the weights of substances deposited at the electrode are proportional to their equivalent weights.

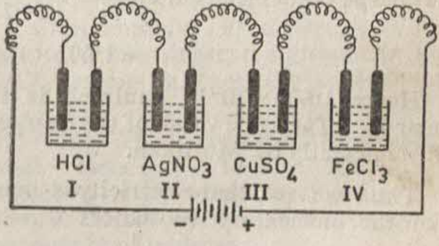


Fig. 11.9

Significance of Faraday's laws. One Faraday, i.e., 96,500 coulombs of electricity liberate at the electrodes equivalent weights of different elements. Since in solution the current is carried by ions and 1 gram-equivalent of ion of any element are discharged and deposited at the electrode by one Faraday or F coulombs of electricity, it follows that 1 gram-equivalent of any ion carries the same quantity of electricity, namely, 1 Faraday. Now, it is known that

1 gram-ion of any element $= n \times 1$ gram-equivalent of the ion

(1 gram-ion is numerically equal to 1 gram-atom) where n is the valency of the element.

Hence, 1 gram-ion of any substance carries n Faraday or nF coulombs of electricity. Now, the number of individual ions which are present in 1 gram-ion is N, i.e., the Avogadro number. Hence, N individual ions carry $n \times \mathrm{F}$ coulombs of electricity. Therefore, every separate ion carries $\frac{n \times \mathrm{F}}{\mathrm{N}}$ coulombs of electricity. Since n is an integer, viz., one for a univalent ion like Na^+, 2 for a bivalent ion like Cu^{++}, 3 for a trivalent ion like Al^{+++} and so on, it follows that charge of a univalent ion (i.e., singly charged ion) $= \frac{\mathrm{F}}{\mathrm{N}}$. (11.15)

Since a univalent ion is produced either by the removal or by addition of an electron from or to neutral atom, we can, therefore, write

$$\text{the charge of an electron, } e = \frac{\mathrm{F}}{\mathrm{N}} = \frac{96{,}494 \text{ coulombs}}{6{\cdot}023 \times 10^{23}}$$

$$= 1{\cdot}602 \times 10^{-19} \text{ coulomb} \qquad (11{\cdot}16)$$

Hence, $1{\cdot}602 \times 10^{-19}$ coulomb is the charge borne by a single electron. The same value of the charge of an electron was obtained experimentally by Mullikan.

Thus we see that electricity is composed of 'atom of electricity' like the elementary substances which are composed of atoms. $\frac{\mathrm{F}}{\mathrm{N}}$ is the "atom" or unit of electric charge which is equal to the charge of an electron. From (11·16) we get F=Ne, i.e., one Faraday of electricity is the charge of an electron multiplied by the Avogadro number. Hence, one Faraday of electricity contains Avogadro-number of electrons, i.e., $6{\cdot}023 \times 10^{23}$ electrons. For this reason, one Faraday is called a *mole of electrons.*

From (11·15) it follows that a monovalent cation is formed by the loss of one electron from an atom, e.g., $K \rightarrow K^+ + e$; similarly, a bivalent cation results from the loss of two electrons, e.g., $Ca \rightarrow Ca^{+2} + 2e$ and so on. Hence, the number of charges carried by an ion is equal to its valence.

The charge carried by different ions is given in the following table :

Table 11.2

Ion	Valency	Charge carried by ion (coulomb)
H^+, Na^+, K^+, Rb^+, Cs^+, Ag^+	1	$1{\cdot}602\times10^{-19}$ (positive charge)
F^-, Cl^-, Br^-, I^-, OH^-, NO_3^-	1	$1{\cdot}602\times10^{-19}$ (negative charge)
Ba^{++}, Sr^{++}, Ca^{++}, Cu^{++}, Zn^{++}	2	$2\times1{\cdot}602\times10^{-19}$ (positive charge)
SO_4^{-2}, SO_3^{-2}	2	$2\times1{\cdot}602\times10^{-19}$ (negative charge)
Fe^{+3}, Al^{+3}	3	$3\times1{\cdot}602\times10^{-19}$ (positive charge)
PO_4^{-3}, BO_3^{-3}	3	$3\times1{\cdot}602\times10^{-19}$ (negative charge)

Exactitude of Faraday's laws. Faraday's laws represent one of the most exact experimental facts in scientific work. The reason for this can be understood as follows :

An electrode reaction is essentially a counting process—a doling out or a removal of a whole number of electrons at each electrode. In the electrolysis of four different substances, viz., HCl, $AgNO_3$, $CuSO_4$ and $FeCl_3$ as in fig. 11.9, the cathode and anode reactions are :

I. Cathode reaction : $H^+ + 1e \rightarrow H^0$, i.e., each H^+ ion removes one electron from the cathode. Hence, $6{\cdot}023\times10^{23}$ electrons are required to deposit one gram-atomic weight of hydrogen, i.e., 1·008 gram of hydrogen. Therefore, $6{\cdot}023\times10^{23}$ electrons are required to deposit one gram-equivalent weight of hydrogen.

II. Cathode reaction : $Ag^+ + 1e \rightarrow Ag^0$, i.e., each Ag^+ ion removes one electron from the cathode. Hence, $6{\cdot}023\times10^{23}$ electrons are required to deposit one gram-atomic weight of silver. Therefore, $6{\cdot}023\times10^{23}$ electrons are required to deposit one gram-equivalent of silver.

III. Cathode reaction : $Cu^{++} + 2e \rightarrow Cu^0$, i.e., each Cu^{++} ion removes two electrons from the cathode. Therefore, $2\times(6{\cdot}023\times10^{23})$ electrons are required to deposit one gram-atomic weight of copper. Now, gram-equivalent weight of copper is equal to its gram-atomic weight divided by two. Hence, $6{\cdot}023\times10^{23}$ electrons are required to deposit one gram-equivalent of copper.

IV. Cathode reaction : $Fe^{+3} + 3e \rightarrow Fe^0$, i.e., each Fe^{+3} ion removes three electrons from the cathode. Hence, $3\times(6{\cdot}023\times10^{23})$

electrons are required to deposit one gram-atomic weight of iron or $6{\cdot}023 \times 10^{23}$ electrons are required to deposit one gram-equivalent weight of iron because one gram-equivalent weight of iron is equal to its gram-atomic weight divided by its valence, i.e., 3.

In general, if M represents an atom of an element, then

$$M^{+n} + ne \rightarrow M \quad \text{where} \quad n = \text{valency of M}$$

Hence, one M^{+n} ion removes n electrons from the cathode. That is, $n \times 6{\cdot}023 \times 10^{23}$ electrons are required to deposit one gram-atomic weight of M. Now, the valency of M is n. Hence, the gram-equivalent weight of the element $= \dfrac{\text{the gram-atomic weight}}{n}$

Hence, $n \times 6{\cdot}023 \times 10^{23}/n$. Or, $6{\cdot}023 \times 10^{23}$ electrons are required to deposit one gram-equivalent of M.

I. At anode : $Cl^- \rightarrow Cl^0 + 1e$, i.e., each Cl^- ion gives one electron to the anode. Therefore, in order to deposit one gram-atomic weight of chlorine, $6{\cdot}023 \times 10^{23}$ electrons are to be given to the anode. Hence, when one gram-equivalent weight of chlorine is deposited to the anode, $6{\cdot}023 \times 10^{23}$ electrons are given to the anode.

II. At anode : $4OH^- \rightarrow 2H_2O + O_2 + 4e$, i.e., during the deposit of two atoms of oxygen at the anode, four electrons are given to the anode. Hence, when one atom is deposited on the anode, two electrons are given to the anode. It follows, therefore, that when one gram-atomic weight of oxygen is deposited on the anode $2 \times (6{\cdot}023 \times 10^{23})$ electrons are given to the anode. Hence, $6{\cdot}023 \times 10^{23}$ electrons are given to the anode when one gram-equivalent weight of oxygen is deposited on the anode.

Thus we see that $6{\cdot}023 \times 10^{23}$ electrons are required to deposit one gram-equivalent weight of any substance. Since $6{\cdot}023 \times 10^{23}$ electrons are present in one Faraday or 96,500 coulombs, it follows that one Faraday of electricity or 96,500 coulombs deposit one gram-equivalent weight of any substance at each electrode. This is Faraday's second law of electrolysis.

The relationship just described above is the basis for the definition of the equivalent weight of an oxidising agent or a reducing agent. In the oxidation-reduction reactions, a specific number of electrons are gained or lost by one formula-weight of a substance. *The gram-equivalent weight of a substance is that weight of the substance which corresponds to the transfer of* $6{\cdot}023 \times 10^{23}$ *electrons, i.e., one mole of electrons.* The amount in grams of any substance liberated in electrolysis by 1 Faraday of electricity or by one mole of electrons is its gram-equivalent weight.

The determination of Avogadro's number. From equation 11.16 we have $e = \dfrac{F}{N}$ or $N = \dfrac{F}{e}$ where N is the Avogadro number, F is one Faraday or 96,500 coulombs (more precisely 96,494 coulombs) and e is the charge borne by a single electron. The charge borne by a single electron has been determined by Mullikan in his *oil drop experiment* to be $1{\cdot}602\times10^{-19}$ coulomb. From these, the Avogadro number can be easily calculated as shown below :

$$N=\frac{96{,}494 \text{ coulombs}}{1{\cdot}602\times10^{-19} \text{ coulomb}}=6{\cdot}023\times10^{23}.$$

Determination of electrochemical equivalent. The E. C. E. of an element is determined by passing a known quantity of electricity through a solution and determining the amount of the element deposited on the electrode.

E. C. E. of silver. The apparatus which is used for the determination of E. C. E. of silver is known as silver coulometer as shown in fig. 11.10. This consists of a platinum crucible which is carefully weighed. 30% solution of silver nitrate is taken into the crucible and a rod of pure silver is dipped into the solution. This rod (X) serves as the anode and is surrounded by a glass vessel (Y) so that no anode slime (i.e., detached pieces of silver) reaches the cathode. The crucible and the silver rod (X) are connected to the negative and positive terminals of the battery respectively. In between the coulometer and the battery, a resistance and an ammeter which measures the current are placed in series. The crucible serves as the cathode.

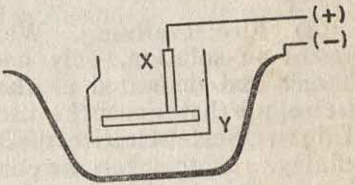


Fig. 11.10

A current of C amperes (which is read from ammeter) is then allowed to pass through the solution for *t* seconds. The deposited silver is washed thoroughly and the platinum crucible and the deposit are dried in air-oven and weighed.

Calculation. Let W grams be the weight of the silver deposited. Since a current of C amperes pass for *t* seconds, the number of coulombs (Q) which pass through the solution is

$$Q=C\times t$$

Hence, Q coulombs of electricity deposit W grams of silver. Hence, by definition,

$$\text{E. C. E. of silver } (Z)=\frac{W}{Q}=\frac{W}{C\times t}$$

from which Z can be found out. The E. C. E. of silver found experimentally is 0·001118 gram.

Conversely, therefore, knowing the amount of silver deposited in silver coulometer, the quantity of electricity passing through the solution can be determined, since 1 coulomb deposits 0·001118 gram of silver.

Some Applications of Electricity in Chemistry. The application of electricity to chemical manufacture produced an industrial revolution. Some of its applications in chemical industries are discussed below :

(1) **Electrolytic production of elements.** Electrochemical processes not only displaced the older methods for the manufacture of such substances as caustic soda and chlorine but made possible the discovery and production of many new elements of great value. Many metals and some non-metals are made by electrolysis of either (i) their salt solution or (ii) their molten or fused compounds. The alkali metals such as sodium, potassium, etc., and the alkaline earth metals such as calcium, magnesium, aluminium, etc., are produced by the electrolysis of their fused compounds. The coinage metals such as copper, silver and gold are obtained by the electrolysis of the solution of their salts. The electrolysis of copper sulphate solution using copper electrodes serves as an example of this process.

(2) **Electrorefining.** When two or more types of ions are present in solution, only one particular type of ions can be discharged and deposited at the electrode under the conditions of electrolysis that hinder the discharge and deposition of other types of ions. Such selective discharge of ions is the basis of electrorefining. Many metals are purified on a large scale in industries by electrorefining. For example, in solution containing copper ion, Cu^{++} and zinc ion, Zn^{++} almost all of the Cu^{++} ions can be discharged and deposited in form of metallic copper at the electrode, under conditions which do not permit the discharge of Zn^{++} ions.

(3) **Electroplating.** One of the earliest applications of electricity was to the electroplating of metals by a process of electrolysis. By electrolysis of a suitable salt solution, it is often possible to deposit a costlier metal as a thin coherent film on the articles constructed of cheaper metal which is made the cathode. Such a process is called electroplating and is widely used to plate a less active metal on a more active one for the purpose of protecting the latter. For example, the articles made up of copper are electroplated with silver. In this process, a solution of potassium argentocyanide is electrolysed, making the article of copper as cathode, the anode being a plate of pure silver :

$$K[Ag(CN)_2] \rightleftharpoons K^+ + [Ag(CN)_2]^-$$

The anion undergoes a slight dissociation :

$$[Ag(CN)_2]^- \rightleftharpoons Ag^+ + 2CN$$

The Ag^+ ions thus formed are deposited on the surface of the cathode as a uniform coherent film of metal. The loss of silver from the electrolyte is compensated by the formation of equivalent quantity of argentocyanide ions by dissolution of silver from the anode. Silver nitrate solution in silver plating cannot be used as electrolyte because the high concentration of silver ions gives rise to the spongy deposit of silver on the cathode instead of the thin film which is required.

Cyanide solutions are also used in the electroplating of gold, zinc, cadmium and other metals. The advantage of these solutions is that they give rise to very small concentrations of the uncomplexed metal ions which favour the production of a uniform thin deposit.

In gold plating, solutions of potassium aurocyanide $K[Au(CN)_2]$ are used in the electroplating bath. The gold ions, Au^+, which are formed as a result of the dissociation of $K[Au(CN)_2]$

$$KAu(CN)_2 \rightleftharpoons K^+ + [Au(CN)_2]^-$$

and $[Au(CN)_2]^- \rightleftharpoons Au^+ + 2CN^-$

are discharged and deposited as a uniform film on the cathode which is made of the material to be gold plated ; the loss of gold from the electrolyte is compensated by the dissolution of gold from the anode.

In the electroplating of rubber, the anode is made up of a metal which is fashioned in the shape of a hand. The anode is dipped into a colloidal solution of rubber ; since rubber colloid is negative ; the rubber particles migrate to the anode and are deposited upon it in the form of a rubber glove. Numerous other articles may be manufactured in a similar process.

(4) **Electrotyping.** A plaster of Paris, wax or gutta percha cast is made of each page of the type and this is coated with graphite to render it a conductor. The cast is then used as the cathode in an electrolytic cell which contains copper sulphate solution ; the anode being a copper plate. Copper metal is deposited as a uniform thin film on the surface of graphitised cast which shows an exact reproduction of every detail of the type or engraving. When a sufficiently thick plate has been formed, it is stripped off. The plate is then strengthened and thickened by filling the back with melted lead.

Books are printed from copper electrotype. Electrotyping is also used in reproducing statues and other works of art.

(5) **Electroanalysis.** The phenomenon of electrolysis can be utilised in the estimation of different metals present in a particular sample or ore. The method consists of selective discharge of ions of metals at the cathode. A metal is deposited at the cathode at a definite voltage ; different metals deposit at different voltage. Hence, by adjusting the voltage, it is possible to separate the different metals by the electrolysis of the solution of their salt in a mixture. The metal which has the lowest deposition voltage (i.e., voltage at which the metal is deposited) is first deposited on the cathode and its weight is determined ; the metal which has the next lowest

deposition voltage, is next deposited, and so on. Thus, when the solution of salts of Cd and Zn is electrolysed, Zinc is first deposited when the voltage is kept at 1 volt, and when all the zinc has been deposited, the voltage is raised to 2 volts at which cadmium is deposited.

Appendix

(a) Distinction between electronic or metallic conductor and electrolyte.

Metallic or electronic conductor	Electrolyte
(i) Metallic conductors conduct electric current without undergoing any chemical change.	During conduction of electric current, electrolytes undergo chemical change.
(ii) In metallic conduction, the conduction is due to loose electrons in the metal. The loose electrons in the metal are pushed from one atom to the next by the potential (or electron pressure) of the battery or generator. As a result there is a flow of a stream of electrons or conduction of current through metallic conductors.	In electrolytic conduction, the current is carried by ions. That is, the electrical circuit obtained when the electrodes dipped in the solution of an eletrolyte are connected to a battery or generator, is maintained unbroken through the solution by the motion and discharge of ions.
(iii) The metallic conductivity decreases with increase in temperature. This is due to the fact that as the temperature increases, the oscillatory motion of the ions increases, impeding the motion of electrons between them.	The electrolytic or ionic conductivity increases with increase in temperature.

(b) Comparison of electrolytic dissociation with thermal dissociation.

Electrolytic dissociation	Thermal dissociation
(i) It is a reversible process, e.g., $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$	It is a reverible process, e.g., $PCl_5 \rightleftharpoons PCl_3 + Cl_2$
(ii) It leads to abnormally low values of molecular weight.	It also leads to abnormally low value of molecular weight.
(iii) The electrolytic dissociation is brought about by the solution of the substance in a suitable solvent or by fusion.	The thermal dissociation is brought about by heating the substance.
(iv) The products of ionic dissociation (i.e., ions of opposite charges) cannot be separated easily because of strong attraction between the oppositely charged ions.	The products of thermal dissociation can be separated by easy mechanical means, e.g., by diffusion, partial solution, etc.
(v) The products of electrolytic dissociation are positive ions and negative ions, the total number of positive charges carried by positive ions being equal to the total number of negative charges carried by negative ions. The solution as a whole, therefore, remains electrically neutral. For example, $NH_4Cl \rightleftharpoons NH_4^+ + Cl^-$	The products of thermal dissociation are neutral molecules, e.g., $NH_4Cl \rightleftharpoons NH_3 + HCl$
(vi) In order to bring about the electrolytic dissociation, the substance is to be dissolved in a suitable solvent, that is, the process requires a medium to take place.	Thermal dissociation does not require a medium and it occurs when the substance is merely heated.

Worked out problems

Ex. 1. A current of 2·5 amperes is passed through a solution of copper sulphate, $CuSO_4$, for 40 minutes, using platinum electrodes. Calculate the weight of each electrolytic product.

Solution. The quantity of electricity that has passed through the solution is given by

$$Q = C \times t$$

Here, $C=2{\cdot}5$ amperes, $t=40$ minutes$=40\times 60=2400$ seconds.

$\therefore\ Q=2{\cdot}5\times 2400=6{,}000$ coulombs.

The equivalent weight of copper$=\frac{63{\cdot}54}{2}=31{\cdot}77$

[valency of copper in $CuSO_4=2$; at. wt. of $Cu=63{\cdot}54$]

Hence, 1 Faraday or 96,500 coulombs of electricity deposit 31·77 grams of copper.

Therefore, the amount of copper deposited at the cathode is

$$W_1=\frac{31{\cdot}77\times 6{,}000}{96{,}500}=1{\cdot}975 \text{ gms.}$$

Similarly, the amount of oxygen liberated at the anode is given by $W_2=\frac{8\times 6{,}000}{96{,}500}=0{\cdot}497$ gm. ($\because$ eq. wt. of oxygen$=8$).

Ex. 2. For how long a time would an electric current of 5 amperes be passed through a solution of an acid in order to liberate 10 litres of hydrogen at N.T.P. ?

Solution. Since the gram-molecular weight, i.e., 2 grams of hydrogen, occupy 22·4 litres at N.T.P., the gram-equivalent weight of hydrogen i.e., 1 gram occupies 11·2 litres at N.T.P.

Hence, the number of gram-equivalent of hydrogen which occupies 10 litres is $\frac{1\times 10}{11{\cdot}2}=\frac{10}{11{\cdot}2}$.

Therefore, the quantity of electricity which liberate $\frac{10}{11{\cdot}2}$ gram-equivalent of hydrogen$=96{,}500\times\frac{10}{11{\cdot}2}=86{,}160$ coulombs.

Now, $Q=C\times t$ or $t=\frac{Q}{C}=\frac{86{,}160}{5}=17232$ seconds. Hence, the time during which the current should be passed is 17232 seconds or 4 hours 47 minutes and 12 seconds.

Ex. 3. For how long a time would a current of 5 amperes have to be passed through a cell containing fused sodium chloride in order to deposit 10 grams of sodium at the cathode ?

Calculate the amount of chlorine which are evolved at the anode.

Solution. Since 1 Faraday or 96,500 coulombs of electricity deposit 1 gram-equivalent, i.e., 23 grams of sodium at the cathode, 10 grams of sodium are deposited by $\frac{96{,}500\times 10}{23}$ coulombs of electricity. Hence, the time in seconds required to deposit 10 grams of sodium is

$$t=\frac{Q}{C}=\frac{96{,}500\times10}{23\times5}=8391{\cdot}0 \text{ seconds.}$$

$$=2 \text{ hours } 19 \text{ minutes } 51 \text{ seconds.}$$

Now, 1 Faraday or 96,500 coulomb of electricity liberate 35·5 grams of chlorine. Hence, the amount of chlorine liberated at the anode$=\frac{35{\cdot}5\times96{,}500\times10}{96{,}500\times23}=15{\cdot}43$ grams.

Ex. 4. A current was passed through a solution of silver nitrate for 5 minutes and 3 grams of silver were deposited at the cathode. What was the current intensity ?

Solution. One gram-equivalent of silver is 107·9 grams. In order to liberate 3 grams of silver $\frac{96{,}500\times3}{107{\cdot}9}$ coulombs of electricity should pass through the solution. Hence, the current intensity was

$$C=\frac{Q}{t}=\frac{96{,}500\times3}{107{\cdot}9\times5\times60}=8{\cdot}94 \text{ amperes.}$$

Ex. 5 What is the equivalent weight of copper if 11·8 grams of the metal are liberated from a solution of copper sulphate by passing electric current of 10 amperes for 1 hour ?

Solution. The quantity of electricity which has passed through the solution during electrolysis is

$$Q=C\times t=10\times60\times60=36000 \text{ coulombs.}$$

Now, 36000 coulombs of electricity liberate 11·8 grams of the metal. Hence, 1 Faraday or 96,500 coulombs of electricity liberate

$$\frac{11{\cdot}8\times96{,}500}{36000}=31{\cdot}6 \text{ grams.}$$

Therefore, the equivalent weight of copper is 31·6.

Ex. 6. The same quantity of electricity which deposited 2·87 grams of a metal liberated 161 c.c. of oxygen collected at 17°C and 754 mm. pressure. Calculate the equivalent weight of the metal.

Solution. Volume of oxygen at N.T.P.

$$=161\times\frac{273}{290}\times\frac{754}{760}=150 \text{ c.c.}$$

Now, 1 c.c. of oxygen at N.T.P. weighs

$$\frac{32}{22{\cdot}4\times1000}=0{\cdot}001429 \text{ gram.}$$

Hence, the weight of oxygen liberated $0{\cdot}001429\times150=0{\cdot}214$ gram.

Now, $\frac{\text{chemical equivalent of metal}}{\text{chemical equivalent of oxygen}}=\frac{\text{weight of metal}}{\text{weight of oxygen}}$.

i.e., $$\frac{\text{equivalent weight of metal}}{8}=\frac{2{\cdot}87}{0{\cdot}214}$$

$$\therefore \text{ The equivalent weight of the metal}=\frac{2{\cdot}87\times 8}{0{\cdot}214}=107{\cdot}3.$$

Ex. 7. A current of 0·02 ampere passed through a solution of a copper sulphate solution for five hours between copper electrodes liberated 0·1177 gram of copper.

Calculate the volume of hydrogen which would be liberated at N.T.P. by the same current for the same time through a dilute solution of sulphuric acid between platinum electrodes. (C.H.S.C.) Also calculate the volume of hydrogen liberated at 27°C and 750 mm pressure.

Solution. The quantity of electricity which has passed through the solution is

$$Q=C\times t=0{\cdot}02\times 5\times 60\times 60=360 \text{ coulombs.}$$

Hence, the equivalent weight of copper $=\frac{0{\cdot}1177\times 96{,}500}{360}=31{\cdot}5.$

Now, $$\frac{\text{weight of copper deposited}}{\text{weight of hydrogen liberated}}=\frac{\text{eq. wt. of copper}}{\text{eq. wt. of hydrogen}}$$

$$\frac{0{\cdot}1177}{\text{weight of hydrogen liberated}}=\frac{31{\cdot}5}{1}$$

(the equivalent weight of hydrogen = 1).

$$\therefore \text{ weight of hydrogen liberated}=\frac{0{\cdot}1177}{31{\cdot}5}=0{\cdot}00374 \text{ grams.}$$

Now, 2 grams of hydrogen (i.e., 1 gram-molecular weight of hydrogen) occupy 22·4 litres at N.T.P. Therefore, the volume occupied by 0·00374 gram of hydrogen is

$$V=\frac{22{\cdot}4\times 0{\cdot}00374}{2}=41{\cdot}9 \text{ c.c.}$$

∴ The volume of hydrogen liberated at 27°C and 750 mm pressure $=\frac{41{\cdot}9\times 760\times 300}{273\times 750}=46{\cdot}65$ c.c.

Ex. 8. An electric current was passed through two cells connected in series. The first cell contains an aqueous solution of silver nitrate and has platinum electrodes. The second cell contains copper sulphate solution and has copper electrodes. After a given time, 608 c c. of oxygen at 25°C and 745 mm pressure has been liberated at the anode of the first cell. Calculate the weights of the metals deposited at other electrodes.

[Eq. wt. of silver = 107·88, Eq. wt. of copper = 31·78.]

Solution. The volume of oxygen at N.T.P.

$$=\frac{745\times608\times273}{760(273+25)}=546 \text{ c.c.} =0{\cdot}546 \text{ litre.}$$

The weight of oxygen at N.T.P. $=\frac{32\times0{\cdot}546}{22{\cdot}4}=0{\cdot}78$ gram.

Now, 1 Faraday of electricity liberate 8 grams of oxygen. Hence, the quantity of electricity which has passed through the solution

$$=\frac{1\times0{\cdot}78}{8}=0{\cdot}0975 \text{ Faraday.}$$

107·88 grams of silver are deposited by 1 Faraday of electricity. Hence, the amount of silver deposited at the cathode of the first cell $=107{\cdot}88\times0{\cdot}0975=10{\cdot}52$ grams. Similarly, the amount of the copper deposited at the cathode of the second cell $=31{\cdot}78\times0{\cdot}0975$ $=3{\cdot}098$ grams. The same amount of copper would be dissolved from the anode of the second cell.

Ex. 9. Two cells one containing silver nitrate solution and the other copper sulphate solution were connected in series. It was found that 0·063 gram of copper was deposited in the same time as 0·216 gram of silver. Determine the equivalent weight of silver. What weight of silver will be deposited when a current of 5 amperes is passed through silver nitrate solution for 10 minutes ?

[Given : eq. wt. of Cu $=31{\cdot}5$.]

Solution : From the second law of Faraday :

$$\frac{\text{equivalent weight of Ag.}}{\text{equivalent weight of Cu.}}=\frac{\text{wt. of Ag deposited}}{\text{wt. of Cu deposited.}}$$

i.e., $\frac{\text{eq. wt. of Ag}}{31{\cdot}5}=\frac{0{\cdot}216}{0{\cdot}063}$.

$\therefore$ equivalent weight of Ag $=\frac{0{\cdot}216\times31{\cdot}5}{0{\cdot}063}=108$.

The quantity of electricity which passes through the silver nitrate solution is,

$$Q=C\times t=5\times10\times60=3000 \text{ coulombs.}$$

Now, 96,500 coulombs of electricity liberate 108 grams of silver.

Therefore, 3000 coulombs of electricity liberate $\frac{108\times3000}{96{,}500}=3{\cdot}357$ grams of silver.

Ex. 10. A current was passed through a cell containing acidulated water and platinum electrodes for 10 minutes. The volume of hydrogen evolved at the cathode is measured at 17°C and 754 mm. pressure to be 161 c.c. Calculate the intensity of the current and also the amount of oxygen liberated at the anode.

Solution. The volume of hydrogen at N.T.P.=

$$161 \times \frac{273}{290} \times \frac{754}{760} = 150 \text{ c.c.}$$

$\therefore$ weight of hydrogen= $150 \times 0{\cdot}00009 = 0{\cdot}0135$ gram. (Since 22·4 litres of hydrogen weigh 2 grams. $\therefore$ 1 c.c. weighs 0·00009 gram.)

Now, water contains 2 volumes of hydrogen and 1 volume of oxygen. Hence, the volume of oxygen which is liberated at the anode=150/2=75 c.c.

$\therefore$ Weight of oxygen$=75 \times \frac{32}{22{\cdot}4 \times 1000} = 0{\cdot}107$ gram.

Now, the quantity of electricity which passes through the solution is,

$$96{,}500 \times 0{\cdot}0135 = 1{\cdot}35 \times 965 = 1302{\cdot}75 \text{ coulombs.}$$

Therefore, the intensity of the current is

$$C = \frac{Q}{t} = \frac{1302\ 75}{10 \times 60} = 2{\cdot}17 \text{ amperes.}$$

Ex. 11. 40 ml of 0·125M $NiSO_4$ solution is electrolysed by a current of 0·05 ampere. How long would this same current have to pass through the solution to remove completely the metal ions from this solution ? [At. wt. of Ni=58·7] [I.I.T., '73]

Solution. 1000 c.c. of 1(M) $NiSO_4$ solution contain 58·7 grams of nickel. $\therefore$ 40 c.c. of 0·125(M) $NiSO_4$ solution contain $\frac{58{\cdot}7 \times 0{\cdot}125 \times 40}{1000}$ gram of nickel. Now, $\frac{58{\cdot}7}{2}$ grams of nickel are deposited by 96,500 coulombs. $\therefore$ $\frac{58{\cdot}7 \times {\cdot}125 \times 40}{1000}$ grams of nickel are deposited by $\frac{96{,}500 \times 2 \times 58{\cdot}7 \times {\cdot}125 \times 40}{58{\cdot}7 \times 1000} = 965$ coulombs.

$\therefore$ Time required to remove completely the metal ions$=\frac{965}{0{\cdot}05}$ seconds or 5 hrs. 21 minutes 40 seconds.

Ex. 12. The electrode reactions for charging of a lead storage battery are :

$$PbSO_4 + 2e^- = Pb + SO_4^{-2}$$

$$PbSO_4 + 2H_2O = PbO_2 + SO_4^{-2} + 4H^+ + 2e^-$$

The electrolyte in the battery is an aqueous solution of sulphuric acid. Before charging, the specific gravity of the liquid was found to be 1·11 (15·7 per cent H_2SO_4 by weight). After charging for 100 hours, the specific gravity of the liquid was found to be 1·28 (36·9 per cent H_2SO_4 by weight). If the battery contained two litres of the liquid, calculate the average current used for charging the battery.

N.B. (e^- denotes electron. Assume that the volume of the battery liquid remained constant during charging). [I.I.T., '72]

Solution. Before charging, 100 grams of solution contain 15·7 grams of H_2SO_4. Or, $\frac{100}{1\cdot11}$ c.c. of solution contain 15·7 grams of H_2SO_4.

$\therefore$ 2,000 c.c. of solution contain $\frac{15\cdot7\times1\cdot11\times2000}{100}=348\cdot54$ grams of H_2SO_4.

Similarly, after charging,

$\frac{100}{1\cdot28}$ c.c. of the solution contain 36·9 grams of H_2SO_4.

$\therefore$ 2000 c.c. of the solution contain $\frac{36\cdot9\times1\cdot28\times2000}{100}=944\cdot64$ grams of H_2SO_4.

$\therefore$ Amount of H_2SO_4 formed$=944\cdot64-348\cdot54=596\cdot1$ grams. Now, 49 grams (gram-eq. wt. of H_2SO_4) of H_2SO_4 are formed by 96,500 coulombs. $\therefore$ 596·1 grams of H_2SO_4 are formed by $\frac{96{,}500\times596\cdot1}{49}$ coulombs.

$\therefore$ Current used$=\frac{96{,}500\times596\cdot1}{49\times100\times60\times60}=3\cdot26$ amperes.

Ex. 13. A current of 1·5 amperes is passed through 4 litres of 1·2(M) copper sulphate solution for two hours. Calculate the weight of product deposited at the electrodes and the strength of acid in normality formed during electrolysis. [H. S., '73]

[At. wt. of Cu$=63\cdot55$]

Solution. Since sulphuric acid is produced, the electrodes used are made up of inert materials such as platinum. Hence, copper is deposited at the cathode and oxygen is liberated at the anode. The quantity of electricity that has passed through the solution $=1\cdot5\times2\times60\times60$ coulombs$=10{,}800$ coulombs. Now, 96,500 coulombs liberate $63\cdot55/2=31\cdot77$ grams of copper. $\therefore$ 10,800 coulombs liberate $\frac{31\cdot77\times10{,}800}{96{,}500}=3\cdot555$ grams of copper. Hence, the amount of copper deposited at the cathode$=3\cdot555$ grams. Similarly, the amount of oxygen liberated at the anode$=\frac{8\times10{,}800}{96{,}500}=0\cdot8952$ grams.

Now, 96,500 coulombs produce 1 gram-equiv. of H^+ ions.

$\therefore$ 10,800 coulombs produce $\frac{1 \times 10{,}800}{96{,}500} = 0\cdot1119$ gram-equivalent of H^+ ions.

Now, 1 gram-equiv. of H^+ ion in 1 litre solution makes its strength 1(N). $\therefore$ 1 gram-equiv. of H^+ ion in 4 litre solution makes its strength $\frac{1}{4}$(N). $\therefore$ 0·1119 gram-equiv. of H^+ ion in 4 litre solution makes its strength $0\cdot1119/4 = 0\cdot027975$(N).

$\therefore$ Strength of acid produced $= 0\cdot027975$(N).

Ex. 14. A current of 10^{-5} amp. is passed through a solution of silver nitrate for 16 minutes and 5 seconds using platinum electrodes. A uniform single-atom thick layer of silver is deposited covering 90% of cathode surface, leaving the rest bare. What is the total surface area of the cathode if each silver atom covers an area of $5\cdot6 \times 10^{-10}$ cm.^{2}? [I.I.T., '68]

Solution. The quantity of electricity passed $= 10^{-5}(16 \times 60 + 5)$ coulomb $= 965 \times 10^{-5}$ coulomb.

Now, 96,500 coulombs deposit 108 grams of silver.

$\therefore$ 965×10^{-5} coulomb deposit $\frac{108 \times 965 \times 10^{-5}}{96{,}500} = 108 \times 10^{-7}$ gram of silver. Now, 108 grams of silver contain $6\cdot023 \times 10^{23}$ atoms of silver. $\therefore$ 108×10^{-7} gram of silver contain $\frac{6\cdot023 \times 10^{23} \times 108 \times 10^{-7}}{108} = 6\cdot023 \times 10^{16}$ atoms of silver.

$\therefore$ surface area of cathode covered by silver $= 5\cdot6 \times 10^{-10} \times 6\cdot023 \times 10^{16} = 5\cdot6 \times 6\cdot023 \times 10^{6}$ sq. cm.

$\therefore$ 90% of the cathode surface $= 5\cdot6 \times 6\cdot023 \times 10^{6}$ sq. cm.

$\therefore$ 100% of the cathode surface $= \frac{5\cdot6 \times 6\cdot023 \times 10^{6} \times 100}{90}$

$= 3\cdot7463 \times 10^{7}$ sq. cm. $\therefore$ Total area of the cathode $= 3\cdot7463 \times 10^{7}$ sq. cm.

Ex. 15. A current of 5 amperes is passed through a copper voltameter and a silver voltameter connected in series for 32 minutes and 10 seconds. Calculate the amount of Cu and Ag deposited. Given E.C.E. of Cu $= 0\cdot000325$ gram and of Ag $= 0\cdot001118$ gram. [C. U. (I. Sc.) '52]

Solution. Amount of Cu deposited $= c \times z \times t = 5 \times 0\cdot000325 \times 1930 = 3\cdot136$ grams. Amount of Ag deposited $= c \times z \times t = 50\cdot001118 \times 1930 = 10\cdot788$ grams.

Ex. 16. 0·2964 gram of copper was deposited on passage of a current of 0·5 ampere for 30 minutes through a solution of copper sulphate. Calculate the atomic weight of copper. [I.I.T., '72]

Solution : Quantity of electricity passed through the solution $=0\cdot5\times30\times60$ coulombs.

Now, $0\cdot5\times30\times60$ coulomb of electricity deposit 0·2964 gram of copper.

Hence, 96,500 coulomb of electricity deposit $\frac{0\cdot2964\times96500}{0\cdot5\times30\times60}$

$=31\cdot78$ gram of copper.

Hence, the equivalent weight of copper $=31\cdot78$

Cathode reaction : $Cu^{++}+2e=Cu$

Hence, the atomic weight of copper $=31\cdot78\times2=63.56$

Ex. 17. For the electrolytic production of $NaClO_4$ from $NaClO_3$ as per the reaction : $ClO_3^-+H_2O \rightarrow ClO_4^-+2H^++2e$, (i) how many Faradays of electricity would be required to produce 1 gram mole of $NaClO_4$; (ii) what volume of H_2 at S.T.P. will be liberated at the cathode in the time that it takes to form 12·25 grams of $NaClO_4$? [I.I.T., '74]

Solution. (i) For each molecule of $NaClO_4$ formed, 2 electrons are liberated. Hence, for the formation of $6\cdot023\times10^{23}$ molecules or 1 gram-mole of $NaClO_4$, $2\times(6\cdot023\times10^{23})$ electrons or 2 moles of electrons are liberated. Now, 2 moles of electrons constitute 2 Faradays of electricity. Hence, 2 Faradays of electricity liberate 1 gram-mole of $NaClO_4$.

(ii) $NaClO_3 + H_2O = NaClO_4 + H_2$

122·5 gram 22·4 litres at N.T.P.

When 122·5 grams of $NaClO_4$ are formed, the volume of hydrogen liberated at N.T.P. is 22·4 litres. ∴ When 12·25 grams of $NaClO_4$ are formed, the volume of hydrogen liberated at N.T.P. is 2·24 litres.

Ex. 18. A current of 0·4825 ampere is passed through a metallic wire. What is the number of electrons passing per second through any point on the wire ? [H. S., '79]

Solution : The quantity of electricity, Q = C (ampere) × t (second)

Hence, the quantity of electricity passing per second $=0\cdot4825\times1$ $=0\cdot4825$ coulomb.

Now, 96500 coulombs of electricity are carried by 1 mole of electrons or $6\cdot023\times10^{23}$ electrons.

∴ 0·4825 coulomb of electricity is carried by $\frac{6\cdot023\times10^{23}\times0\cdot4825}{96,500}$

or $3\cdot011502\times10^{18}$ electrons.

Hence, the number of electrons passing per second through any point of the wire $=3\cdot011502\times10^{18}$ electrons.

Ex. 19. If a current of 2 ampere is passed through copper sulphate solution for 5 minutes, then how many atoms of copper will be deposited at the cathode ? [Cu=63·5]

Solution : The quantity of electricity passed $=2\times5\times60=600$ coulomb.

Equivalent weight of copper $=\frac{63\cdot5}{2}=31\cdot75$

Now, 96,500 coulombs of electricity deposit 31·75 grams of copper.

$\therefore$ 600 coulombs of electricity deposit $\frac{31\cdot75\times600}{96{,}500}$ gram of copper.

Now, 63·5 gram of copper contain $6\cdot023\times10^{23}$ atoms.

$\therefore$ $\frac{31\cdot75\times600}{96{,}500}$ gram of copper contain $\frac{6\cdot023\times10^{23}\times31\cdot75\times600}{63\cdot5\times96{,}500}$ atoms of copper or $1\cdot87\times10^{21}$ atoms of copper.

Hence, $1\cdot87\times10^{21}$ atoms of copper are deposited at the cathode.

Ex. 20. What volume of 0·1(N) H_2SO_4 will be required to neutralise the sodium hydroxide formed when a current of 0·965 ampere is passed through sodium chloride solution for 16 minutes and 40 seconds ?

Solution : The quantity of eletricity passed $=0\cdot965\ (16\times60+40)=965$ coulombs. Equivalent weight of NaOH=40.

Hence, 96,500 coulombs of electricity produce 40 grams of NaOH

$\therefore$ 965 coulombs of electricity produce 0·4 gram of NaOH.

Now, 40 gram of NaOH are neutralised by 1000 c.c. of 1(N) H_2SO_4 solution.

$\therefore$ 0·4 gram of NaOH is neutralised by $\frac{1000\times0\cdot4}{40}=10$ c.c. of 1(N) H_2SO_4 solution.

Again, 10 c.c. of 1(N) H_2SO_4 solution $\equiv$ 100 c.c. of 0·1(N) H_2SO_4 solution.

Hence, in order to neutralise the liberated NaOH 100 c.c. of 0·1(N) H_2SO_4 will be required.

EXERCISES

1. What is the difference between metallic conductor and electrolyte ? Define (a) coulomb, (b) anode and (c) cathode.

2. What happens when copper sulphate solution is electrolysed using (i) copper electrodes and (ii) platinum electrodes ?

3. What are the electrode reactions during the electrolysis of $CuSO_4$, H_2SO_4 and Na_2SO_4 using copper electrodes ?

4. Explain what do you understand by electrolysis? Give illustrations. State Faraday's laws of electrolysis. How would you verify the laws experimentally?

5. Show how would you determine the equivalent weight of an element applying Faraday's laws of electrolysis. What is an electrochemical equivalent of an element? Describe the electrochemical determination of the equivalent weight of copper.

6. Give an account of the theory of electrolytic dissociation. Explain it with examples.

7. What do you mean by one Faraday of electricity? State the significance of Faraday's laws.

8. State the laws of electrolysis. Deduce an equation combining both laws and show how the concept of one Faraday of electricity arises from this equation.

9. Write equations to represent the chemical changes that occur during the electrolysis of each of the following substances : (a) stannous chloride, (b) potassium sulphate, (c) ferric bromide and (d) aluminium sulphate.

10. Describe the following processes :

(a) electrorefining, (b) electroplating and (c) electrotyping.

11. State Faraday's laws of electrolysis and deduce a relation between electrochemical equivalent and chemical equivalent of an element.

12. State the relation between (i) electrochemical equivalent and chemical equivalent of an element. (ii) atomic weight and chemical equivalent of an element. How are these two relations derived from Faraday's laws of electrolysis?

13. Briefly discuss the theory of ionisation. Explain the phenomenon of electrolysis with this theory.

14. Define and illustrate the following :

(a) negative electrode, (b) positive electrode, (c) electrolyte and non-electrolyte, (d) discharge potential.

15. State with reasons whether the following statements are *true* or *false* :

(i) Electrolysis is possible only with electrovalent compounds and not with covalent compounds. [H. S., '78]

(ii) Electrolysis of an aqueous solution of copper sulphate using copper electrodes yields copper at the cathode and oxygen at the anode.

(iii) Molten sodium chloride conducts electricity but anhydrous liquid hydrogen chloride does not. [I. I. T., '67]

(iv) When fused calcium hydride is electrolysed, hydrogen is obtained at the anode. [I. I. T., '73]

(v) Anhydrous hydrogen chloride is a poor conductor of electricity but its aqueous solution is excellent conductor. [I. I. T., '73]

(vi) Sodium is prepared by the electrolysis of molten sodium chloride but not by the electrolysis of aqueous solution. [I. I. T., '73]

(vii) One and two moles of electrons are required to discharge 1 gram-ion and 2 gram-ions of silver and copper respectively.

(viii) Hydrogen chloride when dissolved in water ionises but its ionisation does not occur when dissolved in ether.

(ix) Electrolysis of aqueous solution of $ZnCl_2$ using zinc electrodes yields hydrogen at the cathode.

16. Explain the following statements :

(i) In the electrolysis of aqueous solution of lead nitrate, lead is first deposited on the cathode although lead stands above hydrogen in the electro-potential series.

(ii) One Faraday of electricity is called a mole of electrons.

(iii) One Faraday of electricity deposit one gram-equivalent weight of any element.

(iv) The ratio of one Faraday of electricity to Avogadro number is the charge of an electron.

(v) When zinc is placed in a copper sulphate solution, copper is deposited. (Hints : Copper sulphate solution contains Cu^{++} and SO_4^{--} ions. When zinc is immersed in $CuSO_4$ solution, Zn^{++} ions will go into solution leaving excess of electrons on zinc metal. Cu^{++} ions, being attracted to the negatively charged zinc, take on electrons and become copper atoms).

(vi) The degree of dissociation of an electrolyte increases with dilution.

(vii) Ionisation of an electrolyte does not occur in non-polar solvents but occurs in polar solvents.

(viii) Electrolysis of aqueous solution of sodium chloride using mercury cathode yields sodium on the cathode instead of hydrogen.

(ix) The gram-equivalent weight of a substance is that weight of the substance which corresponds to the transfer of $6{\cdot}023 \times 10^{23}$ electrons.

(x) The relative abilities to act as ionising solvents fall in the order water>acetone>chloroform>benzene.

(xi) One ampere is that amount of current flowing when $1{\cdot}0 \times 10^{-5}$ moles of electrons pass through any cross-section of the conductor in a one-second interval of time.

[Hints : 1 mole of electrons≡96,500 coulombs.

∴ 1 mole of electrons≡96,500 amperes when $t=1$ sec.

∴ 1 ampere of current$\equiv\frac{1}{96{,}500}$ mole$\equiv 1 \times 10^{-5}$ mole of electron].

Problems

Ex. 1. Calculate the amount of silver deposited on the cathode when a current of 10 amperes is passed though the solution of silver nitrate for 10 minutes. (At. wt. of Ag.=107·88) [Ans. 0·67 gram]

Ex. 2. For how long a time would a current of 1·5 amperes have to be passed through copper sulphate solution in order to deposit 3·56 grams of copper at the cathode (Eq. wt. of copper=31·8). [Ans. 2 hours]

Ex. 3. A current was passed through silver nitrate solution for 5 minutes. 2 grams of silver were deposited at the cathode. Calculate the intensity of the current. (Eq. wt. of Ag.=107·9) [Ans. 5·96 amperes]

Ex. 4. If the same electric current passing through two different solutions for the same time liberated 0·840 gram of a metal and 0·0672 gram of oxygen, what is the equivalent weight of the metal ? (Part question N.U.J.B.) [Ans. 100]

Ex. 5. A current of 5 amperes were to be passed through a solution of stannous chloride, $SnCl_2$ for 10 minutes to deposit 1·8466 grams of tin. Calculate the equivalent weight of tin. [Ans. 59·4]

Ex. 6. 19.300 coulombs of electricity were passed through two cells containing Cu_2Cl_2 and $CuCl_2$ solution. Calculate the amount of copper deposited at the cathode of each cell. (At. wt. of copper=63·54) [Ans. 12·708 grams ; 6·354 grams]

Ex. 7. An electric current was passed through two voltameters in series.

Both voltameters were fitted with platinum electrodes; the first contained a solution of a metallic nitrate, the second dilute sulphuric acid. After a given time 0·675 gram of the metal had been deposited on the cathode of the first voltameter and 73·1 c.c. of hydrogen at 16°C and 770 mm pressure had been collected from the cathode of the second. Calculate the equivalent weight of the metal (Cambridge 1st M. B.). [Ans. 107·2]

Ex. 8. A current of 3 amperes when passed through a solution of silver nitrate deposit 2 grams of silver in 10 minutes. Calculate the E. C. E. of silver. [Ans. 0·00111 gram]

Ex. 9. Two cells one containing copper sulphate and the other silver nitrate are set up in series and a current is passed through them. After some time, it is found that 0·945 gram of copper is deposited at the cathode of the first cell and 3·24 grams of silver are deposited at the cathode of the second cell. Calculate the equivalent weight of Cu. Calculate the amount of silver deposited when a current of 5 amperes is passed through the solution of silver nitrate for 10 minutes. Eq. wt. of Ag=108. [Ans. 31·5 ; 0·979 gram]

Ex. 10. A current is passed through two cells connected in series; the first cell contains dil sulphuric acid and has platinum electrodes. The second cell contains copper sulphate solution and has copper electrodes. The current is passed through the solution until 152 c.c. of oxygen at 25°C and 745 mm Hg have been liberated at the anode of the first cell. Calculate the amount of the substance liberated or dissolved at other electrodes. (Eq. wt of copper=31·8).

[Ans. (i) 0·0244 gram of H_2; (ii) 0·7759 gram of copper deposited at cathode. (iii) 0·7759 gram of copper dissolved from the anode.]

Ex. 11. A solution contains Fe^{+2}, Au^{+3}, Hg_2^{++}, Mn^{+2}, Bi^{+3} and Pb^{+2} ions in equal concentrations. In what order, will these ions be discharged during electrolysis?

Ex. 12. Make out schemes for the electrolysis of aqueous solutions of nickelous chloride ($NiCl_2$). potassium iodide (KI), sodium sulphate (Na_2SO_4), barium chloride ($BaCl_2$) and lead nitrate, $Pb(NO_2)_2$.

Ex. 13. A current of 3·7 amperes is passed for 6 hours between nickel electrodes in 0·5 litres of a 2M solution of $Ni(NO_3)_2$. What will be the molarity of the solution at the end of the electrolysis? [I. I. T., '78] [Ans. 2M]

Ex. 14. A current of 10 amperes is passed through a solution of $FeCl_2$ for five minutes and a current of 5 amperes is passed through a solution of $FeCl_3$ for ten minutes. In which case is the amount of iron deposited greater? Justify your answer by calculating the amount of iron deposited in each case. Fe=55·85 [Ans. (i) 0·868 gram. (ii) 0·579 gram]

Ex. 15. Electric current is passed through two cells A and B in series. Cell A contains an aqueous solution of Ag_2SO_4 and platinum electrodes. Cell B contains aqueous solution of $CuSO_4$ and copper electrodes. The current is passed till 1·6 gram of oxygen is liberated at the anode of cell A. (i) Give equations for the reaction taking place at each electrode; (ii) Calculate the quantities of substances deposited at the electrodes of the two cells. [I. I. T., '75] [Ans. Cu=6·35 grams; Ag=21·6 grams]

Ex. 16. A current of 1·5 amperes is passed through a solution of silver nitrate for 1 hour. Calculate the weight of silver deposited on the cathode. [Ans. 6·043 grams] [H. S., '72.]

Ex. 17. Calculate the amount of sulphuric acid formed during the electrolysis of copper sulphate solution if 4825 coulombs are passed through the solution. If the volume of the solution after electrolysis is 500 c.c., what is the strength of the acid in normality? [Ans. 2·45 grams 0·1 (N).]

Ex. 18. When moderately conc. H_2SO_4 is electrolysed, hydrogen is formed at the cathode and peroxydisulphuric acid ($H_2S_2O_8$) at the anode. Write equations which occur at the cathode and anode. [I. I. T., '74]

[Hints : $H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$; at anode : $2HSO_4^- = H_2S_2O_8 + 2e$, etc.]

Ex. 19. A current of 2 amperes is passed through an aqueous solution of copper sulphate through platinum electrodes for 32 minutes and 10 seconds. How much copper will be deposited on the cathode ? [H. S., '71]

(1 Faraday = 96,500 coulombs ; Cu = 63·6) [Ans. 1·272 grams]

Ex. 20. A current of 2 amperes is passed through a solution of a salt of bivalent metal during 80 minutes and 25 seconds. If the weight of the metal deposited at the cathode be 1·2 grams, what is the atomic weight of the metal ? [Ans. 24]

Ex. 21. Calculate the weight of silver deposited on the cathode when a current of 2·5 amperes is passed through a solution of $AgNO_3$ for one hour.

The same current is passed through two other cells, contained in series, one containing a solution of $CuSO_4$ and the other dil. H_2SO_4. Calculate the weight of copper deposited and the volume of hydrogen liberated at N.T.P. (Equivalent weight of Ag and Cu are 107·88 and 31·75 respectively.) [H. S. (Comp.), '67]

[Ans. 10·07 grams of Ag ; 2·961 grams of Cu and 1·044 litres of H_2.]

Ex. 22. How long shall electric current of 5 amperes be passed through a solution of silver salt to coat a surface of 50 square cm. with a layer of 0·008 mm thick, if the density of silver is 10·5 gram/c.c. ? At. wt. of Ag = 108.

[Ans. 1 minute 15 seconds]

[Hints : Volume of Ag deposited = $50 \times 0·0008 = 0·04$ c.c. ∴ Weight of Ag deposited = $0·04 \times 10·5 = 0·42$ grams, etc.]

Ex. 23. An electric current is passed simultaneously through two cells containing (a) acidulated water, and (b) a solution of silver nitrate. Calculate the weight of silver deposited in the second cell during the time that 121·6 ml. of hydrogen at 27°C and 750 mm pressure is liberated in the first. [At. weight of Ag = 107·88, valency of Ag = 1 ; 1 ml. of H_2 at N.T.P. weighs 0·00009 gram].

[Ans. 1·052 gram] [H. S. (Comp.), '65]

Ex. 24. What is the concentration of Ni^{+2} remaining in solution after electrolysis of 1 litre of 0·1 (M) $NiSO_4$ solution by a current of 2 amperes for 20 minutes. The volume of the solution during electrolysis is assumed to remain constant. (Ni = 58·71). [Ans. 0·0876 (M)]

Ex. 25. The same quantity of electricity is passed through acidulated water and through a solution of the sulphate of a metal M. The volume of hydrogen liberated at N.T.P. is 5·56 litres and the weight of the metal deposited is 16·375 grams. If the specific heat of the metal is 0·094, calculate the exact atomic weight of the metal and the molecular formula of the sulphate.

[Ans. 65·5 ; MSO_4]

Ex. 26. 40 ml. of 0·125 M $NiSO_4$ solution is electrolysed by a current of 0·05 ampere for 40 minutes. (i) Write equations for the reactions occuring at each electrode. (ii) How many coulombs of electricity passed through the solution. (iii) How many grams of product deposited on the cathode ? How long would this same current have to pass through the solution to remove completely the metal ions from this solution ? (iv) At the end of electrolysis in (v) how many grams of the product would appear at the anode ? (Ni = 59) [I. I. T., '73]

[Ans. (ii) 120 coulombs. (iii) 0·03668 gram. (iv) 5 hours 21 minutes 40 seconds (v) H_2SO_4 at anode = 0·49 gram ; O_2 at anode = 0·08 gram.]

Ex. 27. When water is electrolysed in a cell hydrogen is liberated at one electrode and oxygen is simultaneously liberated at the other. In a particular experiment, the hydrogen and oxygen so produced were collected together and

the total volume measured 16·8 ml. at N. T. P. How many coulombs were passed through the cell in this experiment ? [I. I. T., '71]
[Ans. 96·5 coulombs]

Ex. 28. In the electrolysis of $CuSO_4$ solution, (a) What weight of copper is deposited on the cathode by a current of 1 ampere flowing for 100 minutes ? (b) What volume of oxygen at N. T. P. is liberated at the anode ? If 500 c.c. of $CuSO_4$ solution is employed in the electrolytic cell, what is the H^+ concentration after electrolysis ? It is assumed that there is no volume change due to electrolysis and the anode reaction is $2H_2O \rightarrow 4H^+ + O_2 + 4e$ [Cu = 63·54].

[Ans. (i) 1·975 gram. (ii) 343 c.c. (iii) 0·124 (N)]

Ex. 29. Calculate the weight of water which may have to be decomposed electrolytically to give enough hydrogen at 27°C and 760 mm pressure to fill a balloon whose capacity is ten million litres. [Ans. $72{\cdot}8\times10^5$ grams]

Ex. 30. A current of 1 ampere is passed through a solution of cupric sulphate for 5 minutes, using Pt-electrodes. Calculate the number of atoms of copper deposited on the cathode. [Ans. $9{\cdot}36\times10^{20}$ atoms.]

[Hints : 2 × 96,500 coulombs deposit $6{\cdot}023\times{}^{23}$ atoms of Cu].

Ex. 31. Calculate the total charge in coulombs carried by the calcium ions in 1 litre of 0·1 (N) $CaCl_2$ solution. $CaCl_2$ is assumed to be completely dissociated in solution. [Ans. 9650 coulombs]

Ex. 32. An acidified solution of copper sulphate was electrolysed between platinum electrodes. 0·1589 gram of copper was deposited at the cathode by passing 0·5 ampere current for 16 minutes 5 seconds. Calculate the value of the Faraday and the charge on the copper ion in coulombs. Write down the reaction occurring at the anode. [I. I. T., '69]

[Ans. 96,450 coulombs, $3{\cdot}2027\times10^{-19}$ coulombs]

Ex. 33. What quantity of zinc in grams should be dissolved per minute in the galvanic cell $Zn/ZnSO_4$—$Cu/CuSO_4$ in order to ensure current intensity of 5 ampere ? [At. wt. of Zn = 65].

[Solution : Equivalent weight of Zn = 65/2 = 32·5. Hence, 32·5 grams of Zn are dissolved by 96,500 coulombs. Now, to ensure the current intensity of 5 ampere, 5 × 60 = 300 coulombs must be passed through the galvanic cell per minute. When 96,500 coulombs are passed through the galvanic cell, the quantity of Zn dissolved = 32·5 grams. So when 300 coulombs are passed, the quantity of Zn dissolved = 32·5 × 300/96,500 = 0·101 grams. ∴ The quantity of Zn dissolved per minute = 0·101 gram.]

Ex. 34. 50 ml of 0·1 (M) $CuSO_4$ solution is electrolysed with a current of 0·965 amp for a period of one minute. The electrode reactions are : Cathode : $Cu^{++} + 2e \rightarrow Cu(s)$; anode : $2H_2O \rightarrow O_2(g) + 4H^+ + 4e$. Assuming that the volume of the solution does not change during electrolysis, calculate the molar concentration of Cu^{++}, H^+ and SO_4^{--} after electrolysis. [I. I. T., '67]

[Hints : 0·965 × 60 coulombs deposit 1 × 0·965 × 60/96,500 = 0·0006 gram-equivalent of Cu^{++}. ∴ Number of moles of Cu^{++} deposited = 0·0006/2 = 0·0003. No. of moles of Cu^{++} before electrolysis in 50 c.c. = 0·1 × 50/1000 = 0·005. ∴ No. of moles of Cu^{++} after electrolysis = 0·005 − 0·0003 = 0·0047. ∴ Concentration of Cu^{++} = 0·0047 × 1000/50 = 0·094 moles/litre. No. of moles of H^+ liberated = 0·0006 and the no. of moles of H^+ before electrolysis is zero. Hence, concentration of H^+ = 0·0006 × 1000/50 = 0·012 moles/litre. Since there is no change in the concentration of SO_4^{--} ion, the concentration of SO_4^{--} = 0·1 mole per litre.].

Ex. 35. The same quantity of current was passed for a period of time through solutions of stannous chloride, $SnCl_2$ and stannic chloride, $SnCl_4$, connected in series. Were the quantities of tin and chlorine liberated from the two solutions equal ? [Ans. No. Amount of Sn from $SnCl_2$ is greater.]

Ex. 36. 96,500 coulombs will liberate 1 gram of hydrogen $(6\times10^{23}$

atoms). Calculate (i) the mass and the number of atoms of silver deposited by 96,500 coulombs from a solution of silver nitrate, (ii) the mass and number of atoms of copper deposited by 96,500 coulombs from copper sulphate solution. [ISC—12, '78]

[Ans. (i) 108 grams, $6{\cdot}023 \times 10^{23}$ atoms, (ii) 31·75 grams ; $3{\cdot}0115 \times 10^{23}$ atoms.

Ex. 37. A current of 2 amperes was passed through an $\frac{N}{10}$ solution of copper sulphate for 16 minutes and 5 seconds. Calculate the amount of copper deposited on the cathode, 96,500 coulombs liberate 31·8 grams of copper.

What will be the effects when the same current is passed (i) through an $\frac{N}{5}$ solution of copper sulphate for the same time and (ii) through $\frac{N}{10}$ solution of the same substance for 32 minutes and 10 seconds ? [H. S., '63]

[**Solution :** The quantity of electricity in coulombs $= 2 \times 965$ coulombs. 96,500 coulombs liberate 31·8 grams. ∴ 2×965 coulombs liberate $31{\cdot}8 \times 2 \times 965/96{,}500 = 0{\cdot}636$ gram of copper. (i) the same quantity (0·636 gram) of copper will be deposited since the quantity of the substance deposited does not depend on the strength of the solution. (ii) Since the time is doubled, the quantity of electricity in coulomb passed through the solution is also doubled. Hence, the quantity of copper deposited will be doubled. (i.e., 1·272 grams.)]

CHAPTER XII

CHEMICAL EQUILIBRIUM

Reversible reactions. A chemical reaction in which the products formed can, in turn. react to regenerate the original substances is called a reversible reaction. For example, if powdered iron is subjected to the action of water vapour at high temperatures, ferrosoferric oxide and hydrogen are formed.

$$3\,Fe + 4H_2O \longrightarrow Fe_3O_4 + 4H_2$$

On the other hand, if hydrogen is passed over ferrosoferric oxide at the same temperature, iron and water are formed

$$Fe_3O_4 + 4H_2 \longrightarrow 3\,Fe + 4H_2O$$

This reaction is, therefore, a reversible reaction. Instead of writing two separate equations, the chemist indicates the reversibility of a chemical reaction by writing a pair of oppositely directed arrows, thus

$$3\,Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2$$

The reaction proceeding from left to right is conventionally called the *forward reaction* and that proceeding from right to left is called the *backward or reverse reaction.*

Not all reactions are reversible in practice. There are many reactions in which the products do not reform the original substances. In such reactions, the initial substances are transformed entirely into the reaction products in which case we say that the reaction is complete. Such reactions are called irreversible reactions. Thus, the reaction $2KClO_3 \rightarrow 2KCl + 3O_2$ is irreversible because KCl and O_2 formed do not recombine to form $KClO_3$. An irreversible reaction proceeds in one direction only.

The rate of chemical reactions. If a piece of sodium is thrown into water, it immediately reacts with water forming sodium hydroxide and hydrogen ; the reaction proceeds so rapidly that sodium bursts into flames and often an explosion results :

$$2Na + 2H_2O = 2NaOH + H_2$$

If a piece of calcium is thrown into water, a vigorous reaction takes place with the liberation of hydrogen and formation of calcium hydroxide :

$$Ca + 2H_2O = Ca(OH)_2 + H_2.$$

On the other hand, if a piece of iron is thrown into water, there is no perceptible reaction. Thus, sodium, calcium and iron react with water with different rates ; the rate of reaction of sodium with water being the highest. By the "rate of a chemical reaction" we mean *the rate at which the concentration of the reacting substances de-*

creases with time. It is usually expressed as the number of moles of the reactants converted to products in one second or one minute or one hour of time. The rate of reaction depends upon a number of external factors such as (i) the nature of the reacting substances, (ii) temperature, (iii) catalytic action and (iv) concentration of the reacting substances.

(i) **The nature of the reacting substances.** The rate of the chemical reaction depends markedly on the nature of the reactants. For example, if hydrogen and fluorine are brought together even at low temperatures, they react with almost explosive violence to form hydrogen fluoride. Hydrogen and chlorine react rapidly at room temperature to produce hydrogen chloride and the reaction is catalysed by sunlight. Hydrogen and bromine react more slowly and the reaction takes place only at elevated temperatures. The reaction of hydrogen and iodine takes place still more slowly and the reaction occurs at still higher temperatures and in the presence of a catalyst such as platinum. Thus, with the same element hydrogen, fluorine, chlorine, bromine and iodine react with different rates. From this fact, it may be concluded that the reaction rate is an inherent property of a reactant.

(ii) **Effect of temperature.** The reaction rate is highly influenced by the temperature. With only relatively few exceptions, the rate of the reactions increases as the temperature is raised. Experiment shows that each 10° rise in temperature approximately doubles or trebles the rate of the majority of the reactions. For example, at room temperature, magnesium combines with oxygen of the air very slowly to form MgO, while if a piece of magnesium is heated, it burns rapidly with a brilliant flame.

As the temperature is increased, the molecules becomes less stable and more active. With rise of temperature, therefore, the relative quantity of active molecules which are more amenable to chemical reaction increases and hence the speed of the reaction increases.

(iii) **Effect of catalysts.** Catalysts change the rate at which chemical reaction occurs. A positive catalyst increases the rate of the reaction while a negative catalyst decreases the reaction rate. For example, MnO_2, acts as a positive catalyst in the decomposition of $KClO_3$ into KCl and O_2. Finely divided metals such as platinum and nickel, or metallic oxides such as ferric and vanadium oxides increase the rate of the combination of SO_2 and O_2 to SO_3.

$$2SO_2+O_2=2SO_3$$

Because of this catalytic action, the manufacture of sulphuric acid by contact process is possible. Catalytic action is specific ; a given catalyst catalyses certain specific reactions. One catalyst which increases the rate of one reaction may have no effect on another. Many reactions of great commercial importance depend on the use of specific catalysts.

(iv) Effect of concentration on the rate of reaction. The law of mass action. The rate at which a chemical reaction takes place depends upon the concentration of the reactants. The chemical reactions occur faster when the concentration of the reacting substances is greater. For example, if a piece of iron wire is heated in air, the iron reacts with oxygen of air to form oxides but only slowly. If, however, a heated iron wire is plunged into a bottle containing pure oxygen, reaction occurs almost violently. Thus, the rate of reaction between iron and oxygen increases since the concentration of oxygen increases. The quantitative relationship existing between reaction rate and concentration was first stated by two Norwegian chemists C. M. Guldberg and P. Waage in 1867. Their statement is known as the *law of mass action.* The law may be stated as follows ; *At constant temperature, the rate of a chemical reaction is directly proportional to the active masses of the reacting substances.* The active mass is defined as the molar concentration, i.e., gram-molecules or moles per litre.

In order to get a mathematical expression of the law of mass action, we shall begin with the simplest reactions in which one molecule of one substance A reacts with one molecule of another B to form one molecule of the substance C. Such reactions can be expressed by the following general equation :

$$A+B=C \qquad (12{\cdot}1)$$

According to the law of mass action, the rate r of this reaction is proportional to the molar concentration of the reactants A and B :

$r \propto [A] \times [B]$, where [A] and [B] represent the molar concentrations of the reactants A and B. Converting the proportionality to an equality, we get

$$r=k\,[A]\times[B] \qquad (12{\cdot}2)$$

where k is a proportionality constant or a constant of proper numerical value known as the rate constant of the reaction. The rate constant k remains invariable for any given reaction at a given temperature and characterises the influence of the nature of the reacting substances on the rate of the reaction between them. The numerical value of k is different at different temperatures.

If $[A]=1$ and $[B]=1$, the equation (12·2) becomes

$$r=k$$

Hence, *the rate constant k is numerically equal to the reaction rate when the molar concentrations of the reactants or their product are equal to unity.*

If the reactants A and B are in the gaseous state, we can substitute the partial pressures for concentrations in equation (12·2) since according to the laws of Avogadro and Dalton, the partial pressure of a gas in a gaseous mixture is proportional to the molar concentration of the gas in the mixture. We then get,

$$r = k_p \times P_A \times P_B \qquad (12{\cdot}3)$$

where P_A and P_B are the partial pressures of A and B respectively and k_p is known as a pressure constant.

Let us consider next less simple reactions in which two molecules of the substance A react with one molecule of substance B to produce one molecule of substance D, thus

$$2A + B = D \quad \text{or} \quad A + A + B = D \qquad (12{\cdot}4)$$

For this reaction to occur, two molecules of A must collide simultaneously with one molecule of B. The rate of this reaction is, therefore, expressed as

$$r \propto [A] \times [A] \times [B]$$

$$\text{or} \quad r = k \times [A] \times [A] \times [B]$$

$$= k \times [A]^2 [B] \qquad (12{\cdot}5)$$

If A and B are gases

$$r = k_p \times P_A^2 \times P_B \qquad (12{\cdot}6)$$

In the general case where m molecules of A react with n molecules of B to form the product E, the equation may be expressed as

$$mA + nB = E.$$

We have the rate equation for this reaction as

$$r = k \times [A]^m \times [B]^n \qquad (12{\cdot}7)$$

If A and B are gases, $r = k_p \times P_A^m \times P_B^n$ $\qquad (12{\cdot}8)$

The above considerations can be illustrated by the following concrete examples :

(i) $H_2 + I_2 = 2HI$. $\qquad r = k \times [H_2] \times [I_2]$

(ii) $2NO + O_2 = 2NO_2$ $\qquad r = k \times [NO]^2 \times [O_2]$

(iii) $I_2 = 2I$ $\qquad r = k \times [I_2]$

(iv) $2HI = H_2 + I_2$ $\qquad r = k \times [HI]^2$

For a reaction that involves solid, the concentration of the solid reactant is assumed to be constant for the reason that only the particles on the surface of the solid are available for the reaction. Therefore, in this case, the rate of the reaction depends on the surface area rather than on the volumetric concentration, i.e., the moles per litre. Hence, if a reaction involves a solid substance together with gaseous and dissolved substances, the rate of the reaction varies only with the concentration of the gaseous and dissolved substances. For example, in the case of combustion of coal

$$C + O_2 = CO_2 \qquad (12{\cdot}9)$$

the rate of the reaction is proportional only to the concentration of oxygen:

$$r=k\times[O_2] \qquad (12\cdot10)$$

Chemical equilibrium—a dynamic steady state. Let us consider a simple reversible reaction represented by the following equation :

$$A+B \rightleftharpoons C+D$$

A concrete example of the reaction of this type is the reaction between carbon dioxide and hydrogen :

$$CO_2(g)+H_2(g) \rightleftharpoons CO(g)+H_2O(g)$$

Let us suppose that we have one mole of the reactant A and one mole of the reactant B in a closed container having a volume of one litre. The substances are maintained at constant temperature, and none of the reactants and products can escape. Initially, there will be no molecule of C and D and no reaction other than the reaction between A and B is possible. The reaction between A and B called the forward reaction ($A+B \rightarrow C+D$) will start at a maximum rate since the concentrations of A and B are at their highest values. The concentrations of A and B must decrease just as soon as any C and D are formed because A and B are used up in the reaction. Therefore, as the reaction proceeds, the concentration of the reacting substances and hence the rate of the forward reaction gradually decreases. Now, as soon as some molecules of C and D accumulate, the reverse or backward reaction ($C+D \rightarrow A+B$) sets in. As the reaction proceeds, the concentration of C and D increases and hence the rate of the backward reaction increases We have thus a system in which the rate of the forward reaction which is maximum initially decreases progressively and the rate of the backward reaction which is zero initially increases continually. Finally, a moment arrives when both rates become equal.

If the initial substances are C and D instead of A and B, similar results will be obtained in the same way. In either case, when the rates of both forward and backward reaction become equal, *chemical equilibrium* is established. From this moment on, the concentrations of all four substances remain unchanged for any length of time provided the conditions are not changed. In the state of chemical equilibrium, there is no cessation of either reaction but both the reactions proceed in opposite directions at the same rate. Molecules of C and D are continuously formed and react to give A and B again but the number of molecules of C and D formed in unit time is equal to the number of molecules of C and D that react to give A and B. The system at chemical equilibrium is, therefore, *a dynamically balanced system and hence a chemical equilibrium is essentially a dynamic equilibrium.*

Fig. 12.1 shows how equilibrium is established in a reversible reaction. At the start, the forward reaction proceeds at the highest rate but the rate of this reaction decreases with time. The rate of the backward reaction is zero at the start but increases with time. Finally, a moment arrives when the rates of both reactions become equal at point O and the system is at equilibrium. From O that is, at equilibrium the two opposing reactions proceed at the same time with the same rate. Chemical equilibrium is attained when the rate of the forward reaction becomes equal to that of the backward reaction.

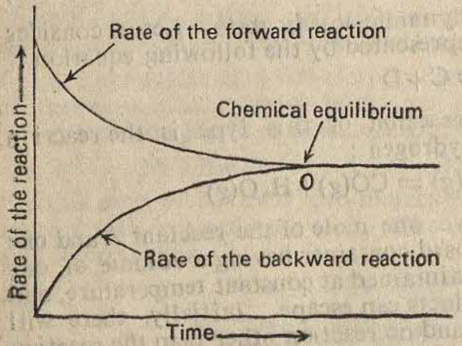


Fig. 12.1

Chemical equilibrium may be defined as the state at which the rate of the backward reaction becomes equal to the rate of the forward reaction and hence the concentrations of the reacting substances do not change.

Now, let us express the condition of equilibrium in mathematical form. Let [A], [B], [C], and [D] represent the molar concentrations of the substances A, B, C and D respectively. Let us suppose that the rate of the forward reaction ($A+B \rightarrow C+D$) is r_f and that of the backward reaction ($C+D \rightarrow A+B$) is r_b. Since the rate of a reaction is proportional to the concentration of the reacting substances, we get for forward reaction

$$r_f \propto [A] \times [B]$$

$$\text{or} \quad r_f = k_f [A] \times [B] \qquad (12{\cdot}11)$$

where k_f is the rate constant of the forward reaction. Similarly, for the backward reaction,

$$r_b \propto [C] \times [D]$$

$$\text{or} \quad r_b = k_b [C] \times [D] \qquad (12{\cdot}12)$$

where k_b is the rate constant of the backward reaction. When equilibrium is established, the rates of the two opposing reactions become equal, that is,

$$r_f = r_b$$

$$\text{or} \quad k_f \times [A] \times [B] = k_b \times [C] \times [D]$$

Rearranging this equation, we get

$$\frac{[C] \times [D]}{[A] \times [B]} = \frac{k_f}{k_b}$$

Since k_f and k_b are constants, their ratio is also a constant so that $\frac{k_f}{k_b}=K$. we then have

$$\frac{[C]\times[D]}{[A]\times[B]}=K. \tag{12·13}$$

where [C], [D], [A] and [B] represent the molar concentrations of the respective substances at equilibrium. The constant K is called the equilibrium constant. The equation (12·13) is the mathematical expression of the law of mass action and is called the equilibrium equation.

The numerical value of equilibrium constant is characteristic of each reaction and does not depend on the concentration. Since the equilibrium constant K is the ratio of the two rate constants k_f and k_b, which change with temperature, K also changes with temperature. Hence, K is a constant only when the temperature remains constant. From equation (12 13), it follows that if the numerical value of K is large, the numerator of the fraction on the left is large, i.e., the concentrations of the products C and D in the equilibrium mixture are large. In other words, if K is large, the forward reaction must have proceeded far towards completion before equilibrium was established. Conversely, if the numerial value of K is small, the denominator of the fraction in the equilibrium equation is large; this means that the concentrations of the reactants A and B in the equilibrium mixture are large. The forward reaction, therefore, did not proceed very far towards completion before equilibrium was established.

If there is a reaction of the type $2A \rightleftharpoons C+D$, we can write it as $A+A \rightleftharpoons C+D$, then the equilibrium equation becomes

$$\frac{[C]\times[D]}{[A]\times[A]}=K$$

$$\text{or,}\quad \frac{[C]\times[D]}{[A]^2}=K \tag{12·14}$$

More generally, for the reaction

$$mA+nB \rightleftharpoons pC+qD.$$

the expression for the equilibrium constant is,

$$\frac{[C]^p\times[D]^q}{[A]^m\times[B]^n}=K \tag{12·15}$$

In general, *for deriving the expressions for the equilibrium constant, we write the product of the concentrations of the substances on the right hand side of the equation in the numerator, and of the substances on the left hand side in the denominator. The concentration of each substance is then raised to a power which is equal to the coefficient preceding the substance in the balanced equation for the reaction.*

If a reaction involves solid substances, their concentrations are not included in the expression for the equilibrium constant. For example, in the case of reaction between carbon dioxide and coal,

$$CO_2 + C \rightleftharpoons 2CO \tag{12·16}$$

the expression for the equilibrium constant is

$$\frac{[CO]^2}{[CO_2]} = K \tag{12·17}$$

When the reactants and products are gases, the partial pressures may be used instead of molar concentrations since the concentration of a gas is proportional to its partial pressure. For the reaction represented by the equation

$$mA(g) + nB(g) \rightleftharpoons pC(g) + qD(g).$$

the expression for the equilibrium constant is

$$\frac{P_C^p \times P_D^q}{P_A^m \times P_B^n} = K_p\ ; \qquad \frac{[C]^p \times [D]^q}{[A]^m \times [B]^n} = K_c \tag{12·18}$$

where K_p is the equilibrium constant ; the subscript "*p*" indicates that K is in terms of partial pressure. The value of K_p is not numerically or dimensionally equal to the value of equilibrium constant expressed in terms of concentration, now designated for distinction as K_c. The relation between the two equilibrium constants K_p and K_c can be deduced as follows :

We have the equation $PV = nRT$, or $P = \frac{n}{V}RT$

or $P = CRT$ where C is the concentration. Hence, in the present case $P_A = [A]\ RT$; $P_B = [B]\ RT$ and so on. We, therefore, have

$$K_p = \frac{P_C^p \times P_D^q}{P_A^m \times P_B^n} = \frac{[C]^p\,(RT)^p \times [D]^q\,(RT)^q}{[A]^m (RT)^m \times [B]^n\,(RT)^n}$$

$$= \frac{[C]^p \times [D]^q}{[A]^m \times [B]^n}\,(RT)^{(p+q)-(m+n)}$$

$$= K_c \times (RT)^{\Delta n}$$

$$\therefore\ K_p = K_c \times (RT)^{\Delta n} \tag{12·19}$$

where $\Delta n = (p+q) - (m+n) =$ the number of moles of the gaseous products minus the number of moles of the gaseous reactants.

For the general reaction, $aA + bB + \ldots \rightleftharpoons mM + nN + \cdots$

$$K_p = \frac{P_M^m \times P_N^n \times \cdots}{P_A^a \times P_B^b \times \ldots} = \frac{[M]^m \times [N]^n \times \ldots}{[A]^a \times [B]^b \times \ldots}\,(RT)^{(m+n+\ldots)-(a+b+\ldots)}$$

$$\therefore\ K_p = K_c (RT)^{\Delta n}$$

Let us now apply this equation to the following examples :

(i) $H_2+I_2 \rightleftharpoons 2HI$; $\triangle n=2-(1+1)=0$ $\therefore$ $K_p=K_c(RT)^0=K_c$

(ii) $2NO+O_2 \rightleftharpoons 2NO_2$; $\triangle n=2-(2+1)=-1$, $\therefore$ $K_p=K_c(RT)^{-1}$

(iii) $N_2+3H_2 \rightleftharpoons 2NH_3$; $\triangle n=2-(1+3)=-2$ $\therefore$ $K_p=K_c(RT)^{-2}$

Thus, we see that for the reactions in which the number of molecules of the products are equal to the number of molecules of the reactant, K_p is equal to K_c. For reactions in which the number of molecules of the reactants are not equal to the number of molecules of the product, $K_p \neq K_c$.

The dimension of K_p and K_c. If in a reaction, there is no change in the number of moles, K_p and K_c have no units, i.e., they are dimensionless. For example, in the reaction $H_2(g)+I_2(g) \rightleftharpoons 2HI(g)$, the total number of moles of the reactants is equal to the total number of moles of products, i.e., there is no change in the number of moles in the reaction. K_c and K_p for this reaction are dimensionless, as is evident from the following calculation :

$$K_c=\frac{[HI]^2}{[H_2][I_2]}=\frac{(\text{mole/litre})^2}{(\text{mole/litre})\times(\text{mole/litre})} \quad \text{and}$$

$$K_p=\frac{P^2_{HI}}{P_{H_2}\times P_{I_2}}=\frac{(\text{atm})^2}{\text{atm}\times\text{atm}}.$$ For this type of reactions, therefore, K_p and K_c have no units.

However, in the reactions in which there is a change in the number of moles, K_p and K_c will have units. For example, in the reaction, $PCl_5 \rightleftharpoons PCl_3+Cl_2$, K_p and K_c have units, as is evident from the following calculation :

$$K_c=\frac{[PCl_3][Cl_2]}{[PCl_5]}=\frac{(\text{mole/litre})\times(\text{mole/litre})}{(\text{mole/litre})}=\text{mole/litre}$$

Thus K_c will have the unit of mole/litre.

$$K_p=\frac{P_{PCl_3}\times P_{Cl_2}}{P_{PCl_5}}=\frac{\text{atm.}\times\text{atm.}}{\text{atm.}}=\text{atm.}$$

Thus K_p will have the unit of atm (or cm or mm)

For the reaction, $N_2+3H_2 \rightleftharpoons 2NH_3$

$$K_c=\frac{[NH_3]^2}{[N_2][H_2]^3}=\frac{(\text{mole/litre})^2}{(\text{mole/litre})\times(\text{mole/litre})^3}=(\text{mole/litre})^{-2}$$

Thus the unit of K_c is $(\text{mole/litre})^{-2}$ or $\text{mole}^{-2}\ \text{litre}^2$.

$$K_p=\frac{P^2_{NH_3}}{P_{N_2}\times P^3_{H_2}}=\frac{(\text{atm.})^2}{(\text{atm.})\times(\text{atm.})^3}=(\text{atm})^{-2}$$

Thus K_p has the unit of $(\text{atm.})^{-2}$.

The equilibrium constant for a reaction in stages. A reaction may be known to occur in several successive steps, by way of intermediate products. For each step we shall get a separate equilibrium constant when equilibrium is attained. For example, the reaction $A+3B \rightleftharpoons AB_3$ may be known to proceed in three separate stages ; for each stage we shall get a separate equilibrium constant :

$$(1)\quad A+B \rightleftharpoons AB\ ;\ K_1=\frac{[AB]}{[A][B]}$$

$$(2)\quad AB+B \rightleftharpoons AB_2\ ;\ K_2=\frac{[AB_2]}{[AB][B]}$$

$$(3)\quad AB_2+B \rightleftharpoons AB_3\ ;\ K_3=\frac{[AB_3]}{[AB_2][B]}$$

If we consider the reaction $A+3B \rightleftharpoons AB_3$ as taking place in a single step, then

$$K_c=\frac{[AB_3]}{[A]\,[B]^3}=\frac{[AB]}{[A]\,[B]}\times\frac{[AB_2]}{[AB]\,[B]}\times\frac{[AB_3]}{[AB_2]\,[B]}=K_1\times K_2\times K_3$$

Thus we see that the concentrations of the intermediate products, AB and AB_2 cancel out. Hence, we need not concern ourselves about the intermediate steps of any reaction and may write the expression for its equilibrium constant as if it occured in a single step as indicated by the chemical equation.

Prediction of the extent of a chemical reaction. The extent to which a chemical reaction goes before equilibrium is attained can be predicted from the magnitude of the numerical value of the equilibrium constant, K. For example, for the reaction $2H_2O(g) \rightleftharpoons 2H_2(g)+O_2(g)$. K_c is $1{\cdot}35\times10^{-11}$ mole/litre at 1703°C. Since the value of K is small, negligible quantities of H_2 and O_2 are present in the epuilibrium mixture. In other words, the reverse reaction $2H_2(g)+O_2(g)\rightarrow 2H_2O(g)$ is practically complete. For this reason, a mixture of H_2 and O_2 is violently explosive and is called a detonating gas. Thus large value of equilibrium constant implies that the equilibrium mixture contains a high proportions of products and the reaction is nearly complete at equilibrium. On the other hand, if the value of equilibrium constant for a reaction is small, the equilibrium mixture contains a low proportions of products and the reaction is far from completion.

Experimental verification of the dynamic nature of chemical equilibrium. That at equilibrium all the chemical reaction has not ceased but both the forward and backward reactions are taking place can be proved by the following experiments : (i) Carbon dioxide reacts with hydrogen to form carbon monoxide and water, and the reaction is reversible :

$$H_2+CO_2 \rightleftharpoons CO+H_2O$$

After the equilibrium has been established, a bit of water from the equilibrium mixture is replaced with heavy water D_2O. After a time besides D_2O, some D_2 and DH are also found in the system, proving that reaction is still occurring even though equilibrium has been established.

(ii) Arsenious acid, H_3AsO_3 is oxidised to arsenic acid, H_3AsO_4, by a solution of iodine in an iodide solution ; iodine being present in such solution as triodide ion, I_3^-. The reaction between arsenious acid and the triodide ion can be represented by the following equation :

$$H_3AsO_3+I_3^-+H_2O \rightleftharpoons H_3AsO_4+3I^-+2H^+$$

When the equilibrium has been obtained, it is necessary to measure the rate of both forward and backward reaction in order to prove that both the opposing reactions are proceeding at the same rate. This has been done with the help of radioactive isotope of arsenic. When pure arsenic is exposed to a beam of neutrons, it is converted into radioactive arsenic from which radioactive arsenious acid can be prepared by the usual method. It is found that radioactive arsenious acid is not converted into radioactive arsenic acid when it is mixed with non-radioactive arsenic acid in solution. When, however, an equilibrium mixture as shown by the above equation is made up with the use of radioactive arsenious acid and non-radioactive arsenic acid, it is found after a time that some radioactive arsenic acid and non-radioactive arsenious acid are present in the system. The rates at which radioactive arsenious acid is converted into radioactive arsenic acid, and at which non-radioactive arsenic acid is converted into non-radioactive arsenious acid are found to be equal and this rate is exactly equal to the rate expected from the law of mass action. This conclusively proves that chemical equilibrium is a dynamic equilibrium in which both forward and backward reactions are going on at equal rates.

Criteria of chemical equilibria. The following are the important criteria of a state of chemical equilibria :

(i) *The equilibrium state is permanent.* A system at equilibrium will remain unaltered in composition for ever, if the external conditions remain the same. That is, if an equilibrium such as $A+B \rightleftharpoons C+D$ is once established, the composition of the equilibrium mixture does not change with time, provided the external conditions such as temperature, pressure, etc., remain unchanged. In other words, the concentrations of A, B, C and D in equilibrium state remain unchanged for any length of time provided the external conditions are not changed.

However, with a change in external conditions such as a change in temperature, the equilibrium state is changed.

(ii) *Chemical equilibrium can be approached from both sides.* We shall illustrate this important characteristic of chemical equilibrium with the help of an example: The hydrogen-iodine reaction is reversible and may be represented as

$$H_2(g)+I_2(g)\rightleftharpoons 2HI(g).$$

If one mole of hydrogen is mixed with one mole of iodine in a closed vessel of one-litre capacity and the vessel is allowed to stand for a long time at 448°C, 1·56 moles of HI are formed. In the equilibrium mixture, there are 1·56 moles of HI, 0·22 mole of H_2 and 0·22 mole of I_2. On the other hand, if two moles of HI are kept in a closed vessel of one-litre capacity and is allowed to stand for a long time at 448°C, 0·44 mole of HI dissociates into H_2 and I_2. In the equilibrium mixture, there are 1·56 moles of HI, 0·22 mole of H_2 and 0·22 mole of I_2. This proves that whether we start with the reactants or with the products, the same state of equilibrium is finally reached. Thus the equilibrium can be attained from both sides.

(iii) *The chemical reaction remains permanently incomplete.* If the reaction becomes complete in any direction, then the concentration of at least one of the substances will be zero, and this makes the value of the equilibrium constant K either zero or infinity (this is evident from the equation for K). In such cases, therefore, K loses its significance. Hence, a reversible reaction is never complete in any direction.

(iv) *The chemical equilibrium is dynamic in nature.* It involves two opposing reactions, viz., backward and forward reactions which proceed simultaneously at equal speeds.

Application of the law of mass action. The application of the law of mass action enables one to calculate simply and accurately the quantitative effect of adding reactants or products to a system in equilibrium.

(i) **Synthesis of ammonia.** Let us consider the equilibrium that is involved in the manufacture of ammonia from nitrogen and hydrogen by the Haber's process:

$$N_2+3H_2\rightleftharpoons 2NH_3$$

Applying the law of mass action to the reaction, we get the equilibrium equation,

$$\frac{[NH_3]^2}{[N_2]\times[H_2]^3}=K$$

The magnitude of the numerical value of K shows how much NH_3 is present in the equilibrium mixture. That is, from the knowledge of the numerical value of K we can have the information that how well we have achieved the objective of forming NH_3 from N_2 and H_2. If the value of K comes out to be very small, the equilibrium mixture is rich in N_2 and H_2 and poor in NH_3. In that case, we shall change the conditions in such a way that the value of K comes out to be large, that is, the equilibrium mixture becomes richer in NH_3.

Let us now see how the equilibrium constant of this reaction is computed. Let us suppose that at a particular temperature 'a' moles of nitrogen and 'b' moles of hydrogen are introduced into a container of volume v litres. Let 'x' moles of nitrogen react. We then get

	N_2	$+ \ 3H_2$	$\rightleftharpoons 2NH_3$
Initial number of moles	a	b	0
Number of moles at equilibrium	$a-x$	$b-3x$	$2x$

Hence, at equilibrium, $[N_2]=\frac{(a-x)}{v}$; $[H_2]=\frac{b-3x}{v}$ and $[NH_3]=\frac{2x}{v}$

The expression for the equilibrium constant becomes,

$$\frac{[NH_3]^2}{[N_2]\times[H_2]^3}=K_c \quad \text{or,} \quad \frac{\left(\frac{2x}{v}\right)^2}{\left(\frac{a-x}{v}\right)\times\left(\frac{b-3x}{v}\right)^3}=K_c.$$

$$K_c=\frac{4x^2v^2}{(a-x)(b-3x)^3} \qquad (12\cdot20)$$

The equilibrium constant, K_p, in terms of partial pressure is given by

$$K_p=\frac{P^2_{NH_3}}{P_{N_2}\times P^3_{H_2}}$$

Now, the total number of moles at equilibrium

$=a-x+b-3x+2x=a+b-2x$

$\therefore$ mole-fraction of $N_2=\frac{a-x}{a+b-2x}$,

mole-fraction of $H_2=\frac{b-3x}{a+b-2x}$

and mole-fraction of $NH_3=\frac{2x}{a+b-2x}$.

If P is the total pressure, then the partial pressures of the gases at equilibrium are,

$$P_{NH_3}=\frac{2x}{a+b-2x}P, \ P_{H_2}=\frac{b-3x}{a+b-2x}P \text{ and } P_{N_2}=\frac{a-x}{a+b-2x}P$$

The expression for K_p is then

$$K_p = \frac{P^2_{NH_3}}{P_{N_2} \times P^3_{H_2}} = \frac{\left(\frac{2x}{a+b-2x}P\right)^2}{\left(\frac{a-x}{a+b-2x}P\right) \times \left(\frac{b-3x}{a+b-2x}P\right)^3}$$

$$= \frac{4x^2(a+b-2x)^2}{(a-x)(b-3x)^3 p^2} \qquad (12{\cdot}21)$$

From equation (12·20) and (12·21), we find that the smaller v is

or, the greater P is, the greater $\frac{4x^2}{(a-x)(b-3x)^3}$

or, $\frac{4x^2(a+b-2x)^2}{(a-x)(b-3x)^3}$ will be, for K_c or K_p is constant at a constant temperature. This means that the amount of nitrogen (the value of x) reacted must be greater, i.e., the yield of NH_3 must be greater. Hence, the decrease of volume or increase of pressure in this system favours the formation of ammonia.

(ii) The hydrogen-iodine reaction. The formation of hydrogen iodide by the reaction between hydrogen and iodine can be represented by the following equation :

	H_2	+ I_2	⇌	$2HI$
Initial number of moles	a	b		0
Number of moles at equilibrium	$a-x$	$b-x$		$2x$

Let us suppose that a mixture of 'a' moles of hydrogen and 'b' moles of iodine is heated in a container of volume v litres until equilibrium is attained. Let $2x$ moles of hydrogen iodide be present in the equilibrium mixture. Therefore, the number of moles of hydrogen and iodine present in the equilibrium mixture is $(a-x)$ and $(b-x)$ respectively. Substituting these values in the equilibrium equation, we get

$$K_c = \frac{[HI]^2}{[H_2] \times [I_2]} = \frac{\left(\frac{2x}{v}\right)^2}{\left(\frac{a-x}{v}\right) \times \left(\frac{b-x}{v}\right)} = \frac{4x^2}{(a-x)(b-x)}$$

The equilibrium constant is thus seen to be independent of volume and pressure and hence K_p and K_c for this reaction are identical.

The expression for the equilibrium constant does not contain volume and pressure terms and hence K_p and K_c for this reaction are identical as is evident from the following calculation :

Total number of moles present at equilibrium

$$= a - x + b - x + 2x = a + b$$

$\therefore$ Mole-fraction of $H_2 = \frac{a-x}{a+b}$, mole-fraction of $I_2 = \frac{b-x}{a+b}$ and mole-fraction of $HI = \frac{2x}{a+b}$. Hence, if P is the total pressure on the system, then the partial pressures of H_2, I_2 and HI are given by

$$P_{H_2} = \frac{a-x}{a+b}P, \quad P_{I_2} = \frac{b-x}{a+b}P \text{ and } P_{HI} = \frac{2x}{a+b}P$$

$$\therefore \quad K_p = \frac{P_{HI}^2}{P_{H_2} \times P_{I_2}} = \frac{\left(\frac{2x}{a+b}P\right)^2}{\left(\frac{a-x}{a+b}P\right) \times \left(\frac{b-x}{a+b}P\right)} = \frac{4x^2}{(a-x)(b-x)}$$

Thus K_p is found to be identical with K_c, and since the expressions of K_c and K_p do not involve volume and pressure, the pressure and volume have no effect on the position of equilibrium.

The decomposition of hydriodic acid is represented by the equation :

	$2HI \rightleftharpoons$	H_2 +	I_2
Initial number of moles	2a	0	0
Number of moles at equilibrium	$2a-2x$	x	x

Let us suppose that 2a moles of hydrogen iodide are heated in a container of v litres until equilibrium is attained. The number of moles of iodine present in the equilibrium mixture is x. Therefore, the number of moles of hydrogen, and hydrogen iodide left in the equilibrium-mixture is x and $(2a-2x)$ respectively. Substituting these values in the equilibrium equation, we get

$$K_c = \frac{[H_2] \times [I_2]}{[HI]^2} = \frac{\frac{x}{v} \times \frac{x}{v}}{\left(\frac{2a-2x}{v}\right)^2} = \frac{x^2}{(2a-2x)^2}$$

Hence, the dissociation of hydrogen iodide does not depend upon pressure or volume.

(iii) Dissociation of phosphorus pentachloride. The dissociation of phosphorus pentachloride vapour into phosphorus trichloride and chlorine results in the following equilibrium.

	$PCl_5\ (g) \rightleftharpoons$	$PCl_3\ (g) +$	$Cl_2\ (g)$
Initial number of moles'	a	0	0
Number of moles at equilibrium	$(a-x)$	x	x

The equilibrium constant expression is

$$K_c = \frac{[PCl_3] \times [Cl_2]}{[PCl_5]}$$

Let us suppose that 'a' moles of PCl_5 are heated at a definite temperature in a container of volume of v litres. Let x represent the number of moles of PCl_5 which dissociate to establish equilibrium. Now, one mole of PCl_5 dissociate to give one mole of PCl_3 and one mole of Cl_2. Hence, x moles of PCl_5 will give x moles of PCl_3 and x moles of Cl_2. Hence, the concentrations of the substances at equilibrium are

$$[PCl_5]=\frac{(a-x)}{v};\ [PCl_3]=\frac{x}{v}\ \text{and}\ [Cl_2]=\frac{x}{v}$$

The expression for the equilibrium constant becomes

$$K_c=\frac{[PCl_3]\times[Cl_2]}{[PCl_5]}=\frac{\frac{x}{v}\times\frac{x}{v}}{\frac{(a-x)}{v}}=\frac{x^2}{(a-x)v} \qquad (12.22)$$

The equilibrium constant in this case is dependent on volume or pressure.

The equilibrium constant in terms of partial pressure, K_p, is given by

$$K_p=\frac{P_{PCl_3}\times P_{Cl_2}}{P_{PCl_5}}$$

Now, total number of moles at equilibrium $=a-x+x+x=a+x$

$\therefore$ mole-fraction of $PCl_3=\frac{x}{a+x}$, mole-fraction of $Cl_2=\frac{x}{a+x}$ and the mole-fraction of $PCl_5=\frac{a-x}{a+x}$. If P is the total pressure of the system, then

$$P_{PCl_3}=\frac{x}{a+x}P,\ P_{Cl_2}=\frac{x}{a+x}P\ \text{and}\ P_{PCl_5}=\frac{a-x}{a+x}P$$

$$\text{Hence, } K_p=\frac{P_{PCl_3}\times P_{Cl_2}}{P_{PCl_5}}=\frac{\left(\frac{x}{a+x}P\right)\times\left(\frac{x}{a+x}P\right)}{\left(\frac{a-x}{a+x}P\right)}=\frac{x^2}{a^2-x^2}P \quad (12{\cdot}23)$$

In equation (12·22), v occurs in the denominator. Hence, the greater v is, the greater $\frac{x^2}{a-x}$ is, since K_c remains constant at constant temperature. This means that the amount of dissociation, x, must be greater. In equation (12·23), P occurs in the numerator.

Hence, the less P is, the greater $\frac{x^2}{a^2-x^2}$ is since K_p remains constant at constant temperature. This means that the amount of dissociation must be greater. Hence, the increase of volume and decrease of pressure in this system results in an increase in the dissociation of PCl_5 and conversely.

(iv) Esterification of ethyl alcohol. The reaction between acetic acid and ethyl alcohol leads to the following equilibrium

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

	CH_3COOH	C_2H_5OH	$CH_3COOC_2H_5$	H_2O
Initial number of moles	a	b	0	0
Number of moles at equilibrium	$a-x$	$b-x$	x	x

The expression for the equilibrium constant is

$$K_c = \frac{[CH_3COOC_2H_5] \times [H_2O]}{[CH_3COOH] \times [C_2H_5OH]}$$

Let 'a' moles of acetic acid and 'b' moles of ethyl alcohol are allowed to react in a container having volume of v litres. Let x moles of acetic acid and x moles of alcohol react to produce x moles of ethyl acetate and x moles of water. Therefore, the concentration of the substances in the equilibrium mixture are

$$[CH_3COOH] = \frac{(a-x)}{v}; \ [C_2H_5OH] = \frac{(b-x)}{v}$$

$$[CH_3COOC_2H_5] = \frac{x}{v} \text{ and } [H_2O] = \frac{x}{v}$$

Substituting these values in the equilibrium equation, we get

$$K_c = \frac{[CH_3COO\,C_2H_5] \times [H_2O]}{[CH_3COOH] \times [C_2H_5OH]} = \frac{\frac{x}{v} \times \frac{x}{v}}{\frac{(a-x)}{v} \times \frac{(b-x)}{v}} = \frac{x^2}{(a-x)(b-x)}$$

This expression does not contain v and hence the equilibrium constant is independent of the total volume of the system.

Heterogeneous equilibrium. In the equilibrium mixture, the substances involved may be either in a single phase or in different phases. Accordingly, the chemical equilibrium may be either homogeneous or heterogeneous. The equilibrium is described as homogeneous when all of the substances present in the equilibrium system are in a single phase. When the substances present in the equilibrium system are in two or more phases, the equilibrium is known as heterogeneous equilibrium. For example, the equilibrium resulting from the reaction between nitrogen and hydrogen in the synthesis of ammonia is a homogeneous equilibrium,

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

since all the substances present in the equilibrium mixture are in one phase, e.g., gaseous phase. On the other hand, the equilibrium attained when carbon dioxide reacts with heated coal is a heterogeneous equilibrium,

$$CO_2(g)+C(s)\rightleftharpoons 2CO(g)$$

since CO_2 and CO are present in gaseous phase while carbon is present in solid phase.

The equilibrium equation is applicable to both homogeneous and heterogeneous equilibrium. In heterogeneous equilibrium involving gases and solids, the concentration of the solid is assumed to be constant. The heterogeneous equilibrium attained when calcium carbonate decomposes can be represented as follows :

$$CaCO_3(s)\rightleftharpoons CaO(s)+CO_2(g)$$

An equilibrium constant can be written as

$$K'=\frac{[CaO]\times[CO_2]}{[CaCO_3]}$$

$$\text{or,}\quad K'\times\frac{[CaCO_3]}{[CaO]}=[CO_2]$$

Since the concentration of $CaCO_3$ and CaO are constant, the term $K'\times\frac{[CaCO_3]}{[CaO]}$ is also a constant. The value of this composite term is taken as the equilibrium constant for the decomposition of calcium carbonate. Thus, $K=[CO_2]$

In terms of partial pressure, $K_p=P_{CO_2}$.

Factors that affect equilibrium. Le Chatelier's principle. In the preceding sections, we have only considered equilibrium system under constant external conditions. The composition of a system at equilibrium can be altered by changing several factors. The most important among these are concentration, pressure and temperature. The general effect of the changes of all these factors upon system at equilibrium is governed by Le Chatelier's principle. Le Chatelier's principle states : *If an external stress (change in temperature, pressure or concentration) is applied to a system in equilibrium, the equilibrium will shift in the direction which tends to undo or diminish the effect of the applied stress.* In other words, if a system at equilibrium is subjected to a change in pressure,

Fig. 12.2 : Le Chatelier.

temperature or concentration, the equilibrium shifts to a new value and a chemical reaction occurs predominantly in that direction which minimises the effect of the external change imposed on the system.

Let us apply Le Chatelier's principle to an equilibrium system represented by the equation,

$$A(g)+3B(g)\rightleftharpoons 2C(g)+X \text{ cal.} \qquad (12{\cdot}24)$$

In this system, the forward reaction is exothermic and hence backward reaction must be endothermic. An actual reaction of this type is the synthesis of ammonia,

$$N_2+3H_2\rightleftharpoons 2NH_3+21{\cdot}88 \text{ kcal.}$$

Effect of temperature. Le Chatelier's principle predicts that if heat is added to a system at equilibrium, the equilibrium should shift in the direction which will lower the temperature, that is, the reaction which proceeds with the absorption of heat will be promoted. In the reaction (12·24) increasing temperature of the equilibrium mixture would favour the backward reaction,

$$2C \rightarrow A+3B$$

which proceeds with the absorption of heat. Increase in temperature, therefore, results in the decomposition of C into more A and B until a new equilibrium is attained. Lowering the temperature causes a shift of equilibrium towards the reaction in which heat is evolved. Hence, in the reaction (12·24) when temperature is lowered, the forward reaction,

$$A+3B\rightarrow 2C$$

would be favoured since it proceeds with the evolution of heat. Decrease in temperature, therefore, results in the increased conversion of A and B into C. Thus, we come to the following conclusion : *On heating an equilibrium system, the equilibrium shifts in the direction of endothermic reaction, while on cooling, the equilibrium shifts in the direction of the exothermic reaction.* There are many chemical reactions which are neither strongly exothermic nor strongly endothermic. In such cases, temperature changes have little effect on the point of equilibrium. However, increase in temperature increases the speed of both forward and backward reaction and hence equilibrium is attained more quickly.

Effect of pressure. When the external pressure exerted on a gaseous system in equilibrium is increased, the equilibrium shifts in the direction of the reaction which decreases the applied pressure. Now in a closed space at constant temperature, the reaction can decrease the pressure only if it leads to a decrease in the total number of molecules of the gaseous substances. In equation (12·24) one molecule of A combines with three molecules of B to form two molecules of C in the forward reaction. Hence, the combination of A and B into C in a closed vessel will obviously cause the pressure to drop. Increasing pressure, therefore, favours the forward reaction with a resultant increased conversion of A and B into C.

On the other hand, when the external pressure is decreased, the equilibrium shifts in the direction of reaction which increases the applied pressure, i.e., which leads to an increase in the total number of molecules of the gaseous substances. In the backward reaction of equation (12·24) two molecules of C decompose to give one molecule of A and three molecules of B. Hence, reduction of pressure favours the backward reaction and C is converted into more A and B. Thus, we get the following version of Le Chatelier's principle in application to the effect of pressure on the equilibrium of reversible gas reactions :

An increase in pressure shifts the equilibrium towards the formation of a smaller number of gas molecules while a decrease in pressure shifts it towards the formation of a larger number of molecules.

If the number of molecules of the gaseous substances does not change, an increase or decrease in pressure will have no effect on the equilibrium. For example, neither increase nor decrease in pressure will disturb the equilibrium represented by the following equation :

$$CO_2+H_2 \rightleftharpoons CO+H_2O.$$

Effect of concentration. If the concentration of one of the substances involved in the equilibrium is increased, the equilibrium shifts in the direction of the reaction which reduces the concentration of the same substance. Thus, in the equation (12·24) if the concentration of A is increased, the equilibrium will shift in that direction which will undo the increased concentration of A, i.e., the forward reaction ($A+2B \rightarrow 2C$) will be promoted. Thus, more C is formed, bringing the concentration of A down again.

On the other hand, decreasing the concentration of any of the substances causes a shift of equilibrium towards the formation of that substance. Thus, if the concentration of A is decreased, the backward reaction ($2C \rightarrow A+2B$) will be favoured causing the formation of more A. *A reaction can, therefore, be made to go to completion by complete removal of one of the products.*

For example, in the reaction between zinc and dil. H_2SO_4 in an open vessel, hydrogen formed is continuously removed from the sphere of action : $Zn+H_2SO_4 \rightarrow ZnSO_4+H_2$. As a result, the reaction continuously proceeds from left to right until it goes to completion. Similarly, the reaction $FeS+2HCl \rightarrow FeCl_2+H_2S$ in an open vessel goes to completion because H_2S formed is continuously removed from the sphere of action. The reaction between sodium chloride solution and silver nitrate solution can be represented as :

$$Na^++Cl^-+Ag^++NO_3^- \rightarrow Na^++NO_3^-+AgCl$$

Ag^+ ions and Cl^- ions are removed from the solution in the form of the precipitates of AgCl and consequently the reaction goes to completion.

In the reaction between sodium hydroxide and hydrochloric acid solution, $Na^+ + OH^- + H^+ + Cl^- \rightarrow Na^+ + Cl^- + H_2O$, H^+ and OH^- ions are removed from the sphere of action due to their combination to form almost unionised molecules of water. Consequently, the reaction between sodium hydroxide and hydrogen chloride solution is practically complete.

Effect of catalyst. When a catalyst is added to a system at equilibrium, it accelerates the forward and backward reaction to the same extent. Hence, a catalyst does not alter the state of equilibrium. However, the role of catalysts in reversible reactions is very great. For reversible exothermic reactions, suitable catalysts are essential to hasten their approach to equilibrium. At low temperatures, the equilibrium between reacting substances is achieved very slowly because the velocity of the reactions is very low at low temperatures The equilibrium would be reached more quickly by increasing the temperature but this shifts the equilibrium in the direction which lowers the temperature. Hence, the endothermic backward reaction will be promoted and the yield of the products of the forward reaction in which we are interested would be very small. *Use of the catalyst permits the rapid attainment of the equilibrium without raising the temperature and hence a better yield of the product is achieved.*

Effect of inert gas on equilibrium. This will depend on the type of reactions.

(i) In reactions in which the number of moles of the reactants is equal to the number of moles of the products, i.e., $\triangle n = 0$, the addition of inert gas has no effect on the state of equilibrium.

(ii) In reactions in which the number of moles of reactants is not equal to the number of moles of products, i.e., $\triangle n \neq 0$, the addition of inert gas has an effect on the state of equilibrium. If, however, an intert gas is added to such a system at constant volume, the equilibrium is not affected in any way. But if an inert gas is added at constant pressure, the state of equilibrium is affected. If $\triangle n$ is positive, addition of an inert gas at constant pressure will favour the product formation. If $\triangle n$ is negative, the addition of an inert gas at constant pressure will favour the formation of reactants. For example, if an inert gas is added at constant pressure to the following equilibrated system

$$SO_2 + \tfrac{1}{2}O_2 \rightleftharpoons SO_3$$

the equilibrium shifts towards the decomposition of SO_3, i.e., the backward reaction, $SO_3 \rightarrow SO_2 + \tfrac{1}{2}O_2$ is favoured.

Applications of Le Chatelier's principle to some reactions

of industrial importance. Let us now consider Le Chatelier's principle in application to some industrial reactions.

(a) Synthesis of ammonia. The synthesis of ammonia from nitrogen and hydrogen is a reversible reaction :

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 + 21{,}880 \text{ cals.}$$

The forward reaction is exothermic to the extent of 21,880 cals. This means that when the reaction proceeds in the forward direction, 10,940 cals of heat are evolved for each mole of NH_3 formed. The backward reaction ($2NH_3 \rightarrow N_2 + 3H_2$) must, therefore, be endothermic and 10,940 cals. of heat are absorbed for each mole of NH_3 decomposed. Now, according to Le Chatelier's principle, lowering the temperature favours the forward reaction and the equilibrium mixture will contain more ammonia. But at low temperature, the speed of the reaction will be very low and a long time is required to form a considerable quantity of ammonia. So the reaction should be conducted at the lowest possible temperature at which the reaction proceeds with a workable speed. This temperature is called the optimum temperature. Above the optimum temperature, the yield of ammonia diminishes owing to the fact that the backward reaction is promoted. Below it, the reaction rate is so low that it would not be profitable to carry out the reaction. The reaction is finally accelerated by the use of catalysts since catalysts have no effect on the final state of equilibrium. The most suitable catalyst is the metallic iron in the form of spongy mass with insignificant admixtures of aluminium and potassium compounds.

The equation shows that the forward reaction ($N_2 + 3H_2 \rightarrow 2NH_3$) results in a decrease in the number of molecules. Therefore, according to Le Chatelier's principle, increasing the pressure should favour the forward reaction, i.e., should favour the formation of ammonia. Hence, the higher is the pressure, the greater is the yield of ammonia. The process is actually conducted at 400 to 550°C and 100 to 1000 atm.

(b) Oxidation of sulphur dioxide to sulphur trioxide. Sulphur dioxide directly unites with oxygen to form sulphur trioxide :

$$2SO_2 + O_2 \rightleftharpoons 2SO_3 + 46{\cdot}8 \text{ kcal.}$$

The reaction is employed in the manufacture of sulphuric acid. The forward reaction is exothermic and hence is promoted at low temperatures. The yield of SO_3 will, therefore, be greater, the lower is the temperature. Too low a temperature would make the reaction too slow. Hence, as low a temperature as will still give us a reasonable reaction rate is used. Further the speed of the reaction is increased by using a catalyst. The most suitable catalyst for this reaction is finely divided platinum or vanadium pentoxide.

Since 3 molecules produce 2 molecules in the forward reaction, this results in a decrease in the total number of molecules in the system. Hence, this reaction results in a decrease in the total pressure that the mixed gases exert. According to Le Chatelier's principle, therefore, an increase in pressure will favour the forward reaction, i.e., the conversion of SO_2 to SO_3.

Raising the oxygen concentration will shift the equilibrium of the reaction to the right and hence the yield of SO_3 will be increased. In practice, the reaction is carried out at 450°C with an excess of oxygen in presence of a catalyst Since the degree of conversion of SO_2 into SO_3 under these conditions is as high as 95—97 per cent, the reaction is conducted at ordinary pressure.

(c) **The formation of nitric oxide.** The combination of nitrogen and oxygen takes place according to the following reversible reaction :

$$N_2 + O_2 \rightleftharpoons 2NO - 43{\cdot}2 \text{ kcal}$$

Since the forward reaction is accompanied by the absorption of heat, it is favoured at high temperatures. Hence, the higher is the temperature, the higher will be the yield of nitric oxide. Since the number of molecules does not change in the reaction, change of pressure has no effect on the equilibrium.

In order to get high yield of nitric oxide, not only high temperature but efficient cooling of the reaction products is essential. If the temperature is lowered slowly, the nitric oxide again decomposes into nitrogen and oxygen and hence the yield of nitric oxide is greatly lowered. For this reason, the reaction product is cooled very quickly so that the equilibrium does not get a chance to shift immediately. It does not shift after cooling due to the very slow rate of the reaction at low temperatures so that almost the entire quantity of NO formed at high temperatures remains in the mixture.

(d) **Synthesis of methanol.** The synthesis of methanol involves the union of carbon monoxide and hydrogen :

$$CO + 2H_2 \rightleftharpoons CH_3OH + \text{heat}$$

The equation shows that one molecule of carbon monoxide reacts with two molecules of hydrogen to form one molecule of methanol. Hence, a decrease in the number of molecules occurs in the forward reaction. At higher pressures, the yield of methanol will, therefore, be greater since according to Le Chatelier's principle the equilibrium is shifted to the right.

For each mole of methanol formed, a considerable quantity of heat is produced. Hence, if heat is added to the equilibrium mixture, the equilibrium will shift to the left according to Le Chatelier's principle. Hence, the yield of methanol will be greater at low temperatures. The reaction is carried out in presence of a catalyst which is a mixture of chromic oxide and zinc oxide.

(e) **Other industrial gas reactions.** The above considerations apply to all other industrial gas reactions such as synthesis of chlorine by Deacon's process, oxidation of ammonia, manufacture of hydrogen, etc.

Problems

Ex. 1. How will the rate of the reaction between sulphur dioxide and oxygen

$$2SO_2+O_2 \rightarrow 2SO_3$$

change, if the volume of gaseous mixture is reduced four times ?

Solution : Let the concentration of sulphur dioxide and oxygen before the change in volume be

$$[SO_2]=x\ ;\ [O_2]=y$$

Hence, before the volume has changed the rate of the reaction is

$$v_1=k\times[SO_2]^2\times[O_2]=k\times x^2\times y$$

when the volume is reduced four times the concentration is increased four times ; we, therefore, get

$$[SO_2]=4x \text{ and } [O_2]=4y$$

Therefore, after reduction in volume, the rate of the reaction is

$$v_2=k\times[4x]^2\times 4y=64kx^2y$$

$\therefore\ v_2=64v_1$, that is, the rate of the reaction has increased 64 times.

Ex. 2. If 0·1 mole of phosphorus pentachloride is vaporised in a total volume of 2 litres at 250°C, it is found that at equilibrium the concentrations of the PCl_5, PCl_3 and Cl_2 are respectively 0·021 mole/litre, 0·029 mole/litre and 0·029 mole/litre.

Calculate the equilibrium constant for the reaction at 250°C.

Solution. The dissociation of phosphorus pentachloride is represented by the following equation :

$$PCl_5 \rightleftharpoons PCl_3+Cl_2$$

The expression for the equilibrium constant is

$$K=\frac{[PCl_3]\times[Cl_2]}{[PCl_5]}$$

Substituting the values of concentrations of the substances at equilibrium, we get

$$K=\frac{0{\cdot}029 \text{ mole/litre}\times 0{\cdot}029 \text{ mole/litre}}{0{\cdot}021 \text{ mole/litre}}$$

$$=0{\cdot}04 \text{ mole/litre.}$$

Ex. 3. When heated, phosphorus pentachloride dissociates according to the following equation

$$PCl_5 \rightleftharpoons PCl_3+Cl_2$$

2 moles of phosphorus pentachloride are decomposed in a closed 10-litre vessel at a temperature at which the equilibrium constant *is*

known to be 0·45. Calculate the number of moles of chlorine produced.

Solution. Let x moles of phosphorus pentachloride react to produce equilibrium. Hence, the number of moles of PCl_5 left at equilibrium is $(2-x)$. Since 1 mole of PCl_5 gives 1 mole of PCl_3 and 1 mole of Cl_2, x moles of PCl_5 will give x moles of PCl_3 and x moles of Cl_2. Hence, the concentration of each of the substance at equilibrium is

$$[PCl_5]=\frac{2-x}{10}\text{ mole/litre. }[PCl_3]=\frac{x}{10}\text{ mole/litre. }[Cl_2]=\frac{x}{10}\text{ mole/litre.}$$

Substituting these values in the expression for the equilibrium constant, we get

$$K=\frac{[PCl_3]\times[Cl_2]}{[PCl_5]}=\frac{\frac{x}{10}\text{ mole/litre}\times\frac{x}{10}\text{ mole/litre}}{\frac{2-x}{10}\text{ mole/litre}}=0{\cdot}45\text{ mole/litre}$$

$$\therefore\quad x=1{\cdot}5\text{ mole.}$$

Hence, the concentration of chlorine is $\frac{1{\cdot}5}{10}\frac{\text{mole}}{\text{litre}}$ or 0·15 mole/litre.

Ex. 4. On heating a mixture of carbon monoxide with chlorine in a closed vessel, the following equilibrium is established :

$$CO+Cl_2 \rightleftharpoons COCl_2$$

How will the rate of the forward and backward reaction change if the pressure is increased three times by reducing the volume of the gas mixture at constant temperature ? Will this change shift the equilibrium ?

Solution. Let us suppose that the concentration of CO, Cl_2 and $COCl_2$ at equilibrium are

$$[CO]=x\ ;\ [Cl_2]=y\text{ and }[COCl_2]=z$$

Before the reduction of volume of the gaseous mixture, the rate of the forward reaction is

$$v_f=k_1\times[CO]\times[Cl_2]=k_1xy$$

while the rate of the backward reaction is

$$v_b=k_2[COCl_2]=k_2\times z$$

When the volume is reduced three times, the concentrations of all the gases are increased three times. Under these conditions, the rate of the forward reaction is

$$v_f'=k_1\times3\times[CO]\times3\times[Cl_2]=9\,k_1xy$$

while the rate of the backward reaction is

$$v_b'=k_2\cdot3\,[COCl_2]=3k_2z$$

Now, $\frac{v_f'}{v_f}=\frac{9\,k_1xy}{k_1xy}=9$, i.e., the rate of the forward reaction has increased nine times.

Again, $\frac{v_b'}{v_b}=\frac{3k_2z}{k_2z}=3$, that is, the rate of the backward reaction has increased three times.

Thus, the forward reaction has increased 9 times while the backward reaction has increased 3 times. Since the equilibrium is attained only when the rate of the forward reaction equals the rate of the backward reaction, the equilibrium will be upset. The equilibrium will be shifted from left to right, i.e., towards the formation of phosgene because the rate of the forward reaction is greater.

EXERCISES

1. What do you mean by (a) reversible reaction and (b) chemical equilibrium ? Give examples.

2. State (a) Law of mas action and (b) Le Chatelier's principle.

What are the conditions necessary for the establishment of chemical equilibrium ? Give an application of Le Chatelier's principle.

3. Distinguish between (a) homogeneous equilibrium and (b) heterogeneous equilibrium. Give examples.

4. Set up the expression for the equilibrium constant for the following reactions :

(a) $4NH_3+5O_2 \rightleftharpoons 4NO+6H_2O$; (b) $2SO_2+O_2 \rightleftharpoons 2SO_3$
(c) $4HCl+O_2 \rightleftharpoons 2H_2O+2Cl_2$ (d) $CuO(s)+H_2(g) \rightleftharpoons Cu(s)+H_2O(g)$
(e) $CuSO_4, 5H_2O(s) \rightleftharpoons CuSO_4, 3H_2O(s)+2H_2O(g)$
(f) $2(CaSO_4, 2H_2O)(s) \rightleftharpoons 2CaSO_4, H_2O(s)+3H_2O(g)$

5. In the equilibrium $2NO+O_2 \rightleftharpoons 2NO_2+$heat ; how will the equilibrium be displaced (a) if oxygen is added ? (b) if oxygen is removed ? (c) if NO_2 is added, (d) if NO_2 is removed ?

6. What is the effect of temperature and pressure on the following equilibrium in which all the equilibrants are gases ?

(a) $N_2+O_2 \rightleftharpoons 2NO-43$ kcal. (b) $2CO+O_2 \rightleftharpoons 2CO_2+135{\cdot}8$ kcal.
(c) $N_2+3H_2 \rightleftharpoons 2NH_3+24$ kcal.

7. What factors affect the value of equilibrium constant ? What influence does a catalyst have upon the state of equilibrium ?

8. Give an experimental proof of the dynamic nature of chemical equilibrium.

Deduce an expression for equilibrium constant for the following reaction :

$$A+B \rightleftharpoons C+D$$

9. Write notes on (a) Le Chatelier's principle, (b) dynamic equilibrium, (c) relation between K_p and K_c.

10. Apply Le Chatelier's principle to the following reactions :

(a) $N_2+3H_2 \rightleftharpoons 2NH_3+24$ kcal (b) $2CO+O_2 \rightleftharpoons 2CO_2+135{\cdot}8$ kcal
(c) $4HCl+O_2 \rightleftharpoons 2Cl_2+2H_2O+28$ kcal (d) $C_2H_4+H_2 \rightleftharpoons C_2H_6+24$ kcal
(e) $PCl_5 \rightleftharpoons PCl_3+Cl_2-30$ kcal (f) $CO+Cl_2 \rightleftharpoons COCl_2-12$ kcal

11. The equilibrium mixture of NO_2(gas)+CO(gas)$\rightleftharpoons CO_2$(gas)+NO(gas) exists at a definite temperature and at a total pressure of 2 atm. (a) If the total pressure be increased to 4 atm, will the amount of products increase,

decrease or remain the same? Explain your answer. (b) If the partial pressure of CO be increased by introducing more CO into the system from outside, how will the amount of products be affected (Answer only in qualitative terms). [H. S., '78]

12. The equilibrium mixture of $H_2(g)+I_2(g) \rightleftharpoons 2HI(g)$ exists at a definite temperature and pressure. The reaction is exothermic. Explain how the amount of the product will be affected by a change in temperature and pressure on the system. State the principle by which it can be explained, [H. S., '79]

13. Discuss the role of a catalyst in a reversible reaction. How is the following reversible reaction $N_2+3H_2 \rightleftharpoons 2NH_3+X$ cal brought to completion.

14. Explain clearly the following statements :

(i) When a solution of sodium chloride is mixed with one of magnesium sulphate, no reaction occurs, while if a solution of barium chloride is mixed with one of magnesium sulphate, a reaction does occur.

(ii) When sodium sulphate and hydrogen chloride solution are mixed, no reaction occurs while on mixing sodium carbonate and hydrogen chloride solution, a reaction does occur.

(iii) If chlorine is added to the equilibrium mixture $PCl_5 \rightleftharpoons PCl_3+Cl_2$, the degree of dissociation of PCl_5 decreases.

(iv) When argon is added at constant pressure to the equilibrium mixture of $SO_3+\frac{1}{2}O_2 \rightleftharpoons SO_3$, the yield of SO_3 decreases.

(v) The solubility of ammonium chloride in water increases with increase of temperature.

(vi) When soda-water bottle is opened, carbon dioxide bubbles out.

(vii) The reaction, $NaOH+HCl \rightarrow NaCl+H_2O$, proceeds towards the formation of almost unionised water molecules.

(viii) The reaction $FeCl_3+3KCNS \rightleftharpoons Fe(CNS)_3+3KCl$, does not go to completion while the reaction $FeS+2HCl=FeCl_2+H_2S$ proceeds to completion under ordinary conditions.

(ix) The melting point of ice decreases with increase of pressure.

(x) The boiling point of a liquid increases with increase of pressure.

(xi) If saturated solution of KCl is added to the equilibrium mixture of $3KCNS+FeCl_3 \rightleftharpoons Fe(CNS)_3+3KCl$, the colour of the solution becomes paler.

15. State whether the following statements are *true* or *false*. Give reasons of your answer.

(a) In a reversible reaction, a catalyst increases the rate of forward and backward reaction to an equal extent.

(b) A chemical equilibrium is static in nature.

(c) The reaction $A+3B \rightleftharpoons C+2D+X$ cal is favoured at higher temperature and lower pressure.

(d) In the dissociation, $CaCO_3 \rightleftharpoons CaO+CO_2$, the equilibrium constant is equal to the partial pressure of carbon dioxide.

(e) In the dissociation, $NH_4Cl \rightleftharpoons NH_3+HCl$, the equilibrium constant, Kp, is equal to the square root of the partial pressure of ammonia.

(f) In the reaction $N_2O_4 \rightleftharpoons 2NO_2$, the Kp and K_c are identical.

(g) The degree of dissociation of acetic acid decreases, when acetic acid solution in water is concentrated by evaporation.

(h) Water-water vapour equilibrium is dynamic in nature.

16. Show that if pressure on the system $N_2+3H_2 \rightleftharpoons 2NH_3$ is doubled, the partial pressure of ammonia increases four times.

17. Show how the degree of dissociation of a gas can be calculated from observations of its vapour density.

18. Prove that when two chemical equations are added, for which the equilibrium constants are K_a and K_b, the equilibrium constant K for the resultant reaction is $K_a \times K_b$.

[Proof : Let us consider the following reactions :

$$A + 2B \rightleftharpoons AB_2 \text{.........(1)}$$

$$AB_2 \rightleftharpoons C + D \text{.........(2)}$$

$$A + 2B \rightleftharpoons C + D \text{.........(3)}$$

The equilibrium constant K_a for the reaction (1) is

$K_a = \frac{[AB_2]}{[A][B]^2}$ and the equilibrium constant K_b for the equation (2) is

$K_b = \frac{[C][D]}{[AB_2]}$. The equilibrium constant K for the reaction (3) which is obtained when the two equations (1) and (2) are added together is

$$K = \frac{[C][D]}{[A][B]^2} = \frac{[C][D]}{[AB_2]} \times \frac{[AB_2]}{[A][B]^2} = K_b \times K_a \ ]$$

19. Calculate K_p and K_c for $N_2 + 3H_2 \rightleftharpoons 2NH_3$ and for $\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightleftharpoons NH_3$. What are the units of K and K_c in both cases.

20. Two solids X and Y are in equilibrium, $X(s) \rightleftharpoons Y(s)$. If the increase in pressure causes the transformation of X into Y, which solid has the larger density. Explain your answer clearly.

Problems

1. At equilibrium in the system $2HI \rightleftharpoons H_2 + I_2$ the concentrations of the equilibrants at a certain temperature were found to be

$[H_2] = [I_2] = 0{\cdot}0231$ mole/litre ; $[HI] = 0{\cdot}17$ mole/litre

Calculate the equilibrium constant for this reaction. [Ans. $1{\cdot}846 \times 10^{-2}$]

2. The reaction between hydrogen and chlorine proceeds according to the following equation : $H_2 + Cl_2 = 2HCl$.

How will the rate of the reaction change if the pressure is increased four times ? [Ans. increases 16 times]

3. The reaction $2NO + O_2 \rightarrow 2NO_2$ is allowed to proceed in a closed vessel. How will the rate of this reaction change if the pressure is doubled ? [Ans. increases 8 times]

4. At equilibrium the concentration of the equilibrants of the reaction $H_2 + I_2 \rightleftharpoons 2HI$ are

$[H_2] = 0{\cdot}50$ mole/litre, $[I_2] = 0{\cdot}10$ mole/litre and $[HI] = 1{\cdot}8$ moles/litre

What were the initial concentrations of hydrogen and iodine ? [Ans. $[H_2] = 1{\cdot}4$ mole/litre. $[I_2] = 1{\cdot}0$ mole/litre]

5. What is the value of $[H_2O]$ in pure water ? [Ans. 55·5 moles/litre]

6. At 1000°C, the dissociation pressure of $CaCO_3$ is 200 mm. Calculate the value of the equilibrium constant K . [Ans. K = 200 m.m.]

GROUP—B

(Inorganic Chemistry)

CHAPTER I

HYDROGEN

Atomic weight, 1·0081 Atomic number, 1

Electronic configuration, $1s^1$

Paracelsus (1493-1541) was the first chemist to make a recorded reference to the element we now call hydrogen. He knew that iron and sulphuric acid react to form a gas. He said that "an air arises which bursts forth like the wind" when iron interacted with sulphuric acid. In 1766, the English chemist Cavendish first ascertained the true nature of the gas and is, therefore, regarded as the discoverer of the element. Lavoisier (1743-1794), a French chemist was the first to prepare hydrogen from water and he named the gas hydrogen (Greek meaning : water producer).

Hydrogen occurs in the free state in very small quantities, mainly in the upper layer of the atmosphere. Free hydrogen occurs in some volcanic gases. Sun, many stars, and nebulae contain large amounts of free hydrogen. It is believed that the source of solar energy is the nuclear conversion of hydrogen into helium.

Hydrogen is very abundant in the form of compound. Water contains 11·19 per cent of hydrogen. It is an essential constituent of all acids, alkalis and of almost all organic compounds. The compounds making up plant and animal tissues contain hydrogen and petroleum and natural gas consist of compounds which contain hydrogen. Altogether hydrogen constitutes approximately one per cent of the earth's crust.

Preparation. Hydrogen can be prepared from many compounds containing chemically combined hydrogen. The chief sources of hydrogen are (1) acids, (2) alkalis and (3) water.

(1) **From acids.** Metals which are more electropositive than hydrogen can liberate hydrogen from acids. Metals which lie above hydrogen in the electro-chemical series (fig. 1.1) only displace hydrogen from acids ; the higher the element in the series, the more vigorous is the liberation of hydrogen. The metals such as copper, gold, mercury, silver and platinum which are below hydrogen in the activity series do not displace hydrogen from acids.

Acids which are generally used are dilute hydrochloric acid and dilute sulphuric acid. Nitric acid is not suitable since it is an active oxidising agent. The following are the typical equations showing the preparation of hydrogen from the action of a metal upon dilute acids :

K
Na
Ca
Mg
Al
Zn
Fe
Sn
Pb
H
Cu
Ag
Au

Fig. 1.1

$Fe + H_2SO_4 = FeSO_4 + H_2$; $Fe + 2HCl = FeCl_2 + H_2$

$2Al + 6HCl = 2AlCl_3 + 3H_2$; $Mg + H_2SO_4 = MgSO_4 + H_2$

Laboratory preparation. Hydrogen is usually prepared in the laboratory by the reaction of granulated zinc with moderately dilute sulphuric acid (1 volume concentrated acid to 5 volumes water) or hydrochloric acid (1 volume concentrated acid to 2 volumes water) :

$$Zn+2HCl=ZnCl_2+H_2 \; ; \quad Zn+H_2SO_4=ZnSO_4+H_2$$

The reaction is slow if zinc is pure. It is, therefore, customary to add a little copper sulphate solution to the acid in order to make a deposit of metallic copper on the surface of the zinc.

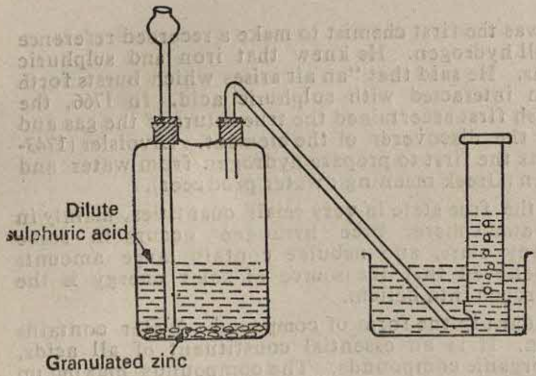


Fig. 1.2 : Preparation of hydrogen.

The apparatus used is a two necked bottle known as woulfe's bottle—so named because these bottles were first described by Peter Woulfe (1784). The two tubulures are fitted tightly with corks through one of which passes a thistle funnel and through the other passes a delivery tube (fig. 1.2). Since a mixture of hydrogen with air is explosive care must be taken to ensure that the apparatus is air-tight. This is tested as follows :

Water is poured down the thistle funnel so that the end of the funnel dips under the surface of water. Then air is blown from the mouth through the delivery tube when water rises up the stem of the thistle funnel. The end of the delivery tube is next closed by the finger. If the level of water in the thistle funnel remains stationary at the same place and does not gradually descend, then the apparatus is air-tight.

Some granulated zinc are then placed into the bottle so that they are covered with water. The end of the delivery tube is put under water in a pneumatic trough. Moderately strong sulphuric acid is then added a little at a time through the thistle funnel until the gas begins to come off vigorously. The gas is allowed to escape for some time in order to drive out all the air from inside the bottle.

In order to collect the gas, a gas-jar is completely filled with water and inverted over water in the trough. The end of the delivery tube is then introduced into the mouth of the gas-jar. Hydrogen collects in the gas-jar by the displacement of water. When the jar is full of hydrogen its mouth is closed with a glass plate while the jar is still under water. The gas-jar is then removed from the pneumatic trough and is kept with its mouth downwards.

Precautions. The following precautions are to be taken during the preparation of hydrogen in the laboratory :

(i) The apparatus must be air-tight.

(ii) The end of the thistle funnel must dip into the acid solution in the woulfe's bottle and the end of the delivery tube must be above the surface of the liquid.

(iii) Before collecting hydrogen all the air from inside the woulfe's bottle must be driven out by allowing hydrogen to escape for some time. To ensure this, a test tube is filled with a sample of gas by the displacement of water and is brought near a flame. If the gas burns without any sound, it is free from air.

(iv) During collection of the gas no air bubble must be allowed to remain in the gas-jar while it is filled with water.

(v) Dilute acids must be used because if zinc is dissolved in concentrated sulphuric acid, the acid is reduced and sulphur dioxide is formed.

$$Zn+2H_2SO_4=ZnSO_4+SO_2+2H_2O$$

Purification. Hydrogen prepared by the laboratory method is not pure. It contains traces of moisture, arsine AsH_3, phosphine PH_3, sulphur dioxide SO_2, carbon dioxide CO_2, hydrogen sulphide H_2S, nitrogen and oxides of nitrogen usually NO_2. The gas is purified by passing it successively through a number of U-tubes connected in series. The U-tubes contain in the following order :

(i) lead nitrate solution to remove hydrogen sulphide H_2S.

(ii) silver sulphate solution to remove arsine and phosphine.

(iii) strong caustic potash (KOH) solution to remove sulphur dioxide SO_2, carbon dioxide CO_2 and nitrogen dioxide NO_2.

(iv) phosphorus pentoxide P_2O_5 to remove moisture or water vapour.

The gas is then collected over mercury and it still contains nitrogen. In order to remove nitrogen, the gas is passed into an evacuated glass bulb containing metallic palladium which is gently heated. Palladium absorbs hydrogen only and nitrogen which remains unabsorbed is pumped out of the bulb. The bulb is then strongly heated when pure hydrogen is evolved. It is collected over mercury.

In spite of these precautions hydrogen is not completely free from all impurities. So it is customary to prepare very pure hydrogen by other methods.

The role of metallic impurities in the preparation of hydrogen by the action of zinc on dil. H_2SO_4 (or dil. HCl). In the laboratory preparation of hydrogen, if zinc employed is highly purified, the liberation of hydrogen begins vigorously but soon slows down. This is due to the fact that a film of hydrogen gas is formed on the surface of zinc and thus prevents zinc from coming in contact with the acid. The liberation of hydrogen gas is essentially the removal of electrons from zinc atoms and their addition to hydrogen ions :

$$Zn \rightarrow Zn^{++} + 2e$$
$$2H^+ + 2e \rightarrow H_2$$

When zinc is placed in dil. acid, zinc goes into the solution as Zn^{++} ions leaving behind two electrons on the zinc surface. The negative charge (layers of electrons) on the zinc metal attracts the H^+ ions formed by the ionisation of the acid. H^+ ions take up these electrons and are converted into hydrogen molecules which form a film of gas on the zinc surface. Zinc is thus prevented from coming in contact with the acid and the evolution of hydrogen gas ceases. If, however, a piece of less active metal such as copper, platinum, etc., is placed in contact with zinc, the metal conducts the liberated electrons away from the zinc surface. Electrons then combine with H^+ ions at a distance from the zinc forming hydrogen molecules which cannot blanket zinc surface and pass away from the solution smoothly. Pairs of metals thus employed are known as *couples.* Usually commercial zinc contains sufficient metallic impurities to be a conglomerate of many small couples. If zinc employed does not contain any metallic impurities, then a little copper sulphate solution is added. Since zinc is more active than copper, it displaces copper from copper sulphate solution and a copper-zinc couple is formed.

(2) **From alkalis.** (i) Like acids many bases contain hydrogen but appear to liberate it much less readily than do acids. Therefore, hydrogen may be prepared by treating certain metals with alkalis. Thus, aluminium reacts with hot concentrated solutions of caustic soda or caustic potash to produce hydrogen :

$$2Al+2NaOH+2H_2O=\underset{\text{(sodium aluminate)}}{2NaAlO_2}+3H_2$$

Zinc and tin also undergo the similiar reaction.

$$Zn+2NaOH=\underset{\text{(sodium zincate)}}{Na_2ZnO_2}+H_2$$

$$Sn+2NaOH=\underset{\text{(sodium stannite)}}{Na_2SnO_2}+H_2.$$

(ii) **Silicol process.** When powdered silicon or ferrosilicon which is an alloy of iron and silicon is heated with a concentrated solution of sodium hydroxide, hydrogen is evolved. This method of preparing hydrogen is known as silicol process.

$$Si+2NaOH+H_2O=2H_2+\underset{\text{(sodium silicate)}}{Na_2SiO_3}$$

The filling of military balloons with hydrogen was once greately facilitated by this reaction. Hydrogenite which is a mixture of ferrosilicon, caustic soda and slaked lime is sold compressed in cakes contained in metal cartridges and when ignited it forms sodium and calcium silicates with the evolution of hydrogen.

(3) **From water.** The chief source of the preparation of hydrogen is water. The following are the different methods of preparing hydrogen from water :

(i) **Electrolysis of water.** When acidulated water is electrolysed, hydrogen is liberated at the cathode and oxygen at the anode.

(ii) **Action of metals on water.** (a) **Action of active metals on cold water.** The very active alkali metals such as lithium, sodium and potassium and the alkaline earth metals such as calcium and barium react with water and liberate hydrogen. With the alkali metals, the reaction is violent and even explosive. For example, when a piece of sodium is dropped into a dish of water, a violent reaction ensues ; the sodium darts, sputtering to and fro over the surface of the water, liberating hydrogen. During this reaction, so much heat is evolved that sodium melts into a ball which rapidly diminishes in size and soon disappears altogether. The reaction between sodium and water can be represented by the equation :

$$2Na+2H_2O=2NaOH+H_2$$

The reaction of water with potassium is more violent and so much heat is evolved that hydrogen liberated bursts into flame.

$$2K+2H_2O=2KOH+H_2$$

Calcium also reacts with water, but with less vigor. The equation for this reaction is

$$Ca+2H_2O=Ca(OH)_2+H_2$$

Calcium hydroxide $Ca(OH)_2$ formed is not very soluble in water and a white precipitate of it is formed during the reaction.

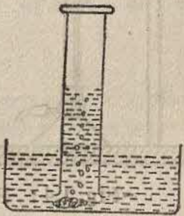


Fig. 1.3 : Action of metallic sodium and metallic calcium on water.

In order to collect hydrogen which is liberated when sodium reacts with water, a piece of sodium is held under water by wrapping it in lead gauze, and kept directly beneath the gas-jar full of water. The hydrogen liberated collects in the gas-jar by the displacement of water. Water becomes alkaline due to sodium hydroxide which is formed during the reaction.

(b) **Action of metals on boiling water.** Magnesium powder decomposes boiling water slowly liberating hydrogen :

$$Mg+2H_2O=Mg(OH)_2+H_2$$

Amalgamated magnesium decomposes cold water while the metal has no appreciable action on cold water.

Amalgamated aluminium which is made by rubbing aluminium foil with damp mercuric chloride rapidly decomposes boiling water with the liberation of hydrogen :

$$2Al+6H_2O=2Al(OH)_3+3H_2$$

Zinc-copper couple decomposes hot water with the evolution of hydrogen :

$$Zn+2H_2O=Zn(OH)_2+H_2$$

Zinc-copper couple is made by pouring a solution of copper sulphate over granulated zinc. Copper deposits on zinc and the resulting product is washed with water to free from adhering salts.

(c) **Action of red-hot metals on steam.** When steam is passed over red-hot magnesium, zinc or iron, it is decomposed with the evolution of hydrogen.

$$Mg+H_2O=MgO+H_2\ ;\ Zn+H_2O=ZnO+H_2$$

$$3Fe+4H_2O\rightleftharpoons Fe_3O_4+4H_2$$

The oxides of the metals are formed instead of hydroxide since all common hydroxides except NaOH and KOH are decomposed at high temperatures, e.g., $Mg(OH)_2\rightleftharpoons MgO+H_2O$.

The reaction of hot iron with steam can be demonstrated in the laboratory with apparatus shown in fig. 1.4.

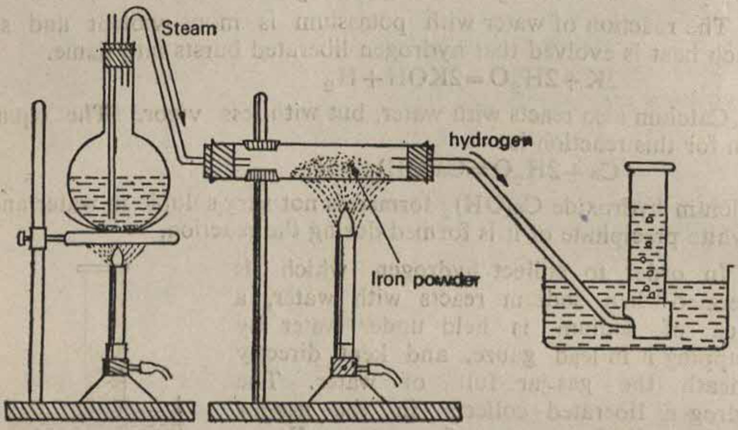


Fig. 1.4 : Preparation of hydrogen by the action of steam on red-hot iron.

Powdered iron is placed in a porcelain tube and heated to redness. Steam is passed by boiling water in a flask over the red-hot iron through the tube. Hydrogen evolved passes through the delivery tube connected at the other end of the tube and collects in a gas-jar by the displacenat of water.

(iii) **Action of steam on coke.** Steam when passed through a bed of hot coke decomposes to produce hydrogen :

$$C+H_2O\rightleftharpoons CO+H_2$$

The resulting mixture of carbon monoxide CO and hydrogen is known as water gas and can be used as gaseous fuel. The carbon monoxide is converted almost completely into carbon dioxide by adding more steam and passing the mixture at about 500°C over a suitable catalyst such as iron oxide.

$$CO+H_2O\rightleftharpoons CO_2+H_2$$

(iv) **Action of steam on a hydrocarbon.** Hydrocarbons from natural gas such as methane and propane react with steam in the presence of nickel as a catalyst to produce hydrogen.

$$\underset{\text{(methane)}}{CH_4} + 2H_2O = 4H_2 + CO_2$$

$$\underset{\text{(propane)}}{C_3H_8} + 3H_2O = 7H_2 + 3CO$$

$$\underset{\text{(propane)}}{C_3H_8} + 6H_2O = 10H_2 + 3CO_2$$

(v) **Action of hydrides on water.** Hydrogen can be prepared by the reaction of a metallic hydride (a compound of a metal and hydrogen) with water. Hydrides of the active and moderately active metals decompose cold water readily to yield hydrogen. With calcium hydride, the reaction is represented by the following equation :

$$CaH_2 + 2H_2O = 2H_2 + Ca(OH)_2$$

Calcium hydride also called hydrolith is most commonly used because it is the cheapest commercially.

(4) **The decomposition of hydrocarbon.** Thermal decomposition of hydrocarbons such as methane, CH_4, under proper conditions forms hydrogen.

$$CH_4 = C + 2H_2$$

Acetylene C_2H_2, is decomposed by electric sparks to yield hydrogen :

$$C_2H_2 = 2C + H_2$$

(5) **The decomposition of ammonia.** Hydrogen can be obtained by the thermal decomposition of ammonia gas over a catalyst at about 500°C :

$$2NH_3 \rightleftharpoons N_2 + 3H_2$$

Compression and shipment of the hydrogen gas requires heavy and expensive equipment. Hence, ammonia is liquefied and shipped to some chemical firm where hydrogen is needed. Ammonia is then decomposed to recover hydrogen.

Preparation of very pure hydrogen. Very pure hydrogen is best prepared in the laboratory by electrolysis of water solution of barium hydroxide. Solution of pure barium hydroxide in distilled water is taken in a hard glass U-tube fitted with nickel electrodes. The U-tube on the side of the cathode is connected with a bulb tube containing platinised asbestos ; the bulb tube is again connected with tubes, one of which contains caustic potash and the other contains pure redistilled phosphorus pentoxide (fig. 1.5). The solution of barium hydroxide in the U-tube is warmed by placing the U-tube in a beaker of hot water ; the two electrodes are then connected to the two poles of a battery when current passes through the solution. Hydrogen evolved passes over platinised asbestos which is heated when the traces of oxygen which hydrogen contains is converted into water. The moisture is then removed by drying the gas first by caustic potash and then by pure redistilled phosphorus pentoxide. The dry and pure

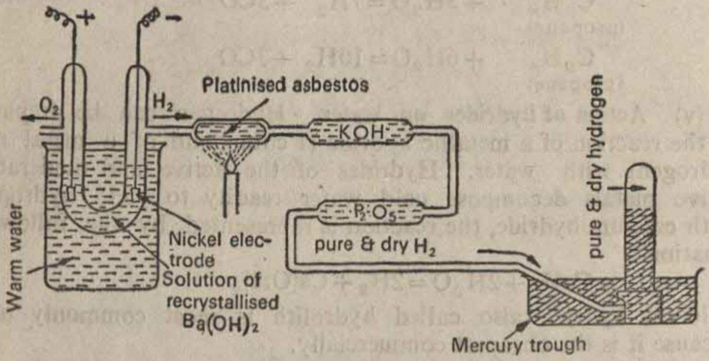


Fig. 1.5 : Preparation of very pure hydrogen.

hydrogen is then collected over pure and dry mercury. If the gas still contains a little nitrogen, it is passed into an evacuated bulb containing metallic palladium which is gently heated. Palladium absorbs hydrogen and not nitrogen which is pumped out. The bulb is then strongly heated when very pure hydrogen is evolved. The gas is then collected over pure and dry mercury.

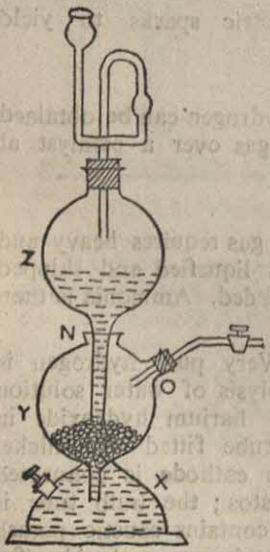


Fig. 1.6 : Kipp's generator.

Preparation of hydrogen in Kipp's generator. Kipp's generator is a device which is useful in the preparation of any gas by the action of a liquid on a coarse solid. In the laboratory, it is necessary to get a ready supply of hydrogen for occasional use. For this purpose, Kipp's generator is usually used. The apparatus is illustrated in fig. 1.6. The two lower glass globes X and Y are joined by a narrow neck and are in communication. The upper globe Z is provided with a long stem and is fitted air-tight into the neck N of the middle globe with its stem reaching almost bottom of the lowest globe. In the upper part of the middle globe, there is an aperture O into which fits tightly a glass tube provided with a stopcock. The bottom globe X is provided with an outlet for the removal of the waste products.

Into the middle globe Y, granulated zinc is introduced through the aperture O. The dilute acid is poured into the upper globe Z so that it also fills the lowest globe X and is driven into the central globe where it comes in contact with the zinc and the reaction takes place. Hydrogen evolved passes through the aperture O.

When the evolution of gas is to be stopped, the stopcock is at once closed. The gas which continues to be evolved in Y cannot pass out ; it collects in the central globe ; exerts pressure on the acids and drives it from the globe Y into the lowest globe X. Part of the acid then rises up the stem into the topmost globe Z. When there is no more acid in the middle globe Y, the gas evolution stops.

When the gas is again required, the stop cock is opened ; the gas passes through the aperture O and the pressure is relieved. The acid rises into the middle globe Y ; comes in contact with zinc again ; more gas is generated and the cycle is repeated.

Properties of hydrogen. (A) **Physical properties.** (i) Hydrogen is a colourless, odourless and tasteless gas. It exists as diatomic molecule, H_2.

It is very slightly soluble in water so that it can be collected over water. Below $-240°C$ hydrogen can be converted under pressure into a colourless liquid. If this liquid is rapidly evaporated solid hydrogen results as colourless crystals melting at $-259{\cdot}4°C$.

Hydrogen is the lightest of all gases ; it is 14·5 times lighter than air. Because of their extreme lightness, hydrogen molecules diffuse at a great rate. This property permits the gas to escape rapidly from a cracked container.

Experiment to prove that hydrogen is lighter than air. Experiment—1. A jar is filled with hydrogen and closed with a cover glass. A jar full of air is now inverted over the jar of hydrogen and the cover glass from the mouth is removed. Hydrogen from the lower jar moves upwards and collects in the upper jar by the downward displacement of air (fig. 1.7). If a lighted taper is introduced into the upper jar it is found that the gas burns with a pale blue flame. This shows that hydrogen moves from lower jar and collects into upper jar. This is possible only when hydrogen is lighter than air.

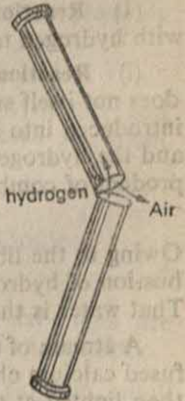


Fig. 1.7

Experiment—II. A rubber balloon is filled with hydrogen gas and released in air. The balloon rises up in the air.

(ii) **Occlusion of hydrogen.** A number of metals have the ability to absorb hydrogen. This phenomenon of absorption of hydrogen by certain metals is known as occlusion of hydrogen. Among these metals are iron, nickel, gold, platinum and palladium which absorb a large volume of hydrogen at ordinary temperature. Of all the metals, palladium has the highest ability to absorb hydrogen ; one milliliter of palladium can absorb upto 900 ml. of the gas. When the metal which contains occluded hydrogen is heated, hydrogen is released again. This fact is made use of in the purification of hydrogen.

The occluded hydrogen is much more reactive than ordinary hydrogen ; it rapidly reacts with oxygen whereas ordinary hydrogen is scarcely affected by ordinary oxygen. When hydrogen is allowed to impinge upon finely divided platinum exposed to the air, hydrogen becomes so active and so much heat is generated by the absorption of the gas that the mixture of hydrogen and oxygen ignites. This principle is utilised in the construction of certain automatic gas lighter.

(B) **Chemical properties.** Under normal conditions, hydrogen is not very reactive chemically. At room temperature, it reacts with almost no other elements unless the reaction is catalysed. But under proper conditions, it combines directly with most elements.

(1) **Reaction with non-metals.** Almost all the non-metals react with hydrogen to form hydrides.

(i) **Reaction with oxygen.** Hydrogen burns in oxygen or air but does not itself support combustion. Thus, when a lighted taper is introduced into an inverted jar of hydrogen, the taper is extinguished and the hydrogen burns at the mouth with a pale blue flame. The product of combustion is water.

$$2H_2+O_2=2H_2O.$$

Owing to the liberation of large amount of heat during the combustion of hydrogen, hydrogen flame has a very high temperature. That water is the product of combustion may be shown as follows :

A stream of hydrogen is passed through a U-tube containing fused calcium chloride to ensure that it is quite dry. The gas is then lighted at the jet attached to the other limb of the U-tube. The gas ignities and burns with a pale blue flame. The flame is allowed to impinge upon the outer surface of the retort (fig. 1.8) which is kept cold by circulating water through it. Drops of a colourless liquid form on the surface of the retort and fall into a beaker placed below it. The liquid turns anhydrous copper sulphate blue proving that it is water.

If a mixture of two volumes of hydrogen and one volume of oxygen is ignited, the gases combine almost instantaneously throughout the volume of the mixture causing a violent explosion. For this reason, this mixture is called *detonating gas*. At ordinary temperature, mixture of hydrogen and oxygen does not react ; it only reacts explosively when heated above 550°C.

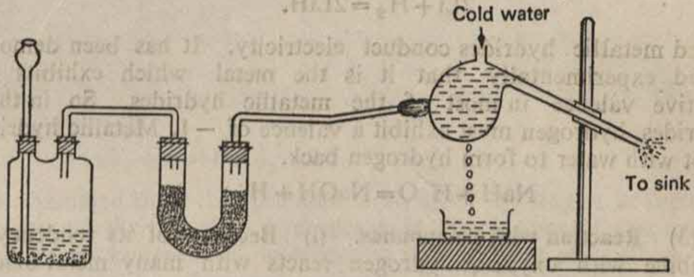


Fig. 1.8 : Hydrogen burns in air to form water.

The reaction between hydrogen and oxygen is catalysed by certain catalysts. For instance, when a piece of platinised asbestos (i.e., a piece of asbestos coated with finely divided platinum) is introduced into a mixture of hydrogen and oxygen, the reaction between the gases is so greatly accelerated that they soon explode to form water.

(ii) **Reaction with halogens.** Hydrogen combines explosively with fluorine even at −25°C.

$$H_2+F_2=2HF$$

Hydrogen burns in chlorine and a mixture of hydrogen and chlorine will explode when heated or when exposed to direct sunlight. Hydrogen chloride is formed.

$$H_2+Cl_2=2HCl.$$

Hydrogen combines less readily with bromine and iodine.

$$H_2+Br_2=2HBr \; ; \quad H_2+I_2=2HI$$

Except for the reactions with iodine, all these reactions are exothermic. The reaction of hydrogen with iodine is endothermic.

(iii) When hydrogen gas is bubbled into boiling sulphur, a foul smelling gas, hydrogen sulphide, is formed.

$$H_2+S=H_2S$$

(iv) Hydrogen combines directly with nitrogen at high pressures and at high temperatures over a crtalyst to form ammonia.

$$N_2+3H_2\rightleftharpoons 2NH_3$$

(2) **Reaction with metals.** Hydrogen combines with active metals such as lithium, potassium, sodium, calcium, etc., when strongly heated to form hydrides.

$$2Na+H_2=2NaH\ ;\quad Ca+H_2=CaH_2\ ;$$
$$2Li+H_2=2LiH.$$

Fused metallic hydrides conduct electricity. It has been demonstrated experimentally that it is the metal which exhibits the positive valence in most of the metallic hydrides. So in these hydrides, hydrogen must exhibit a valence of −1. Metallic hydrides react with water to form hydrogen back.

$$NaH+H_2O=NaOH+H_2$$

(3) **Reaction with compounds.** (i) Because of its tendency to combine with oxygen, hydrogen reacts with many metal oxides. In these reactions, it acts as a reducing agent and the metal oxide is reduced to free metal and hydrogen is oxidised to water.

$$CuO+H_2=Cu+H_2O$$
$$Fe_3O_4+4H_2=3Fe+4H_2O$$

The oxide to be reduced is usually heated to redness in a tube through which the gas is permitted to flow slowly (fig. 1.9). Water vapour and excess hydrogen are raleased at E.

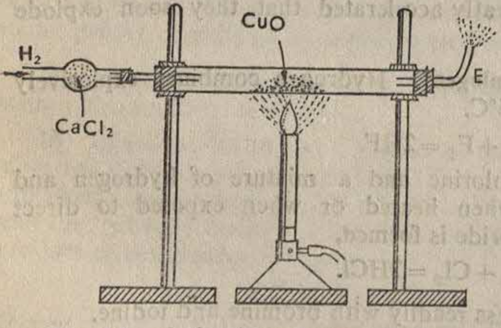


Fig. 1.9 : Reduction of copper oxide by hydrogen.

The oxides of strongly electropositive elements such as lithium, sodium, potassium, etc., are not reduced by hydrogen but on the contrary these metals liberate hydrogen from water.

When hydrogen reacts with metal chlorides, the metal chloride is not usually reduced to the free metal, but to a lower positive state of oxidation. In these reactions, hydrogen chloride is always formed. Thus titanium tetrachloride $TiCl_4$ reacts with hydrogen at about 700°C to form titanium trichloride and hydrogen chloride :

$$2\overset{+4}{Ti}Cl_4+H_2=2\overset{+3}{Ti}Cl_3+2HCl$$

Under suitable conditions hydrogen reacts with carbon monoxide to form various compounds of great value. Thus methanol is prepared on a large scale by the direct union of carbon monoxide and hydrogen in presence of a catalyst :

$$CO+2H_2=CH_3OH \text{ (methanol).}$$

Nascent hydrogen. If a stream of hydrogen is passed through a solution of ferric chloride, no reaction takes place and ferric chloride remains unchanged. Now, if hydrochloric acid is added to a solution of ferric chloride and a piece of zinc dropped into the solution, the hydrogen liberated rapidly converts ferric chloride into ferrous chloride :

$$FeCl_3+H=FeCl_2+HCl.$$

It is assumed that the peculiar activity of hydrogen in such cases is due to the fact that hydrogen is in newly born or nascent state. Nascent hydrogen is hydrogen at the moment of its liberation, when it exhibits abnormal activity. That nascent hydrogen is more reactive and a more powerful reducing agent than ordinary molecular hydrogen can be shown by the following experiments :

(i) To a yellow solution of ferric chloride, hydrochloric acid and a piece of zinc are added. The yellow colour of the solution changes to green which is the characteristic colour of ferrous chloride.

$$2HCl+Zn=ZnCl_2+2H$$

$$2FeCl_3+2H=2FeCl_2+2HCl$$

When hydrogen from kipp's apparatus is passed through another solution of yellow ferric chloride, no change of yellow colour takes place. Hence, ordinary molecular hydrogen does not react with ferric chloride.

(ii) A little potassium permanganate is dissolved in water when a pink coloured solution results. A portion of this solution is acidified with sulphuric acid and hydrogen from kipp's apparatus is passed through it. The pink colour of the solution does not undergo any change.

To another portion of the same solution, pieces of zinc and sulphuric acid are added. The pink colour of the solution gradually disappears due to the reduction of potassium permanganate by the nascent hydrogen formed by the reaction of zinc and sulphuric acid.

$$5Zn+5H_2SO_4=5ZnSO_4+10H$$

$$2KMnO_4+3H_2SO_4+10H=K_2SO_4+2MnSO_4+8H_2O$$

(iii) When hydrogen from kipp's apparatus is bubbled through a solution of arsenic trichloride, no reaction takes place. If to another solution of arsenic trichloride, zinc and hydrochloric acid are added, reaction at once takes place and arsenic trichloride is reduced to arsine :

$$3Zn + 6HCl = 6H + 3ZnCl_2$$
$$AsCl_3 + 6H = AsH_3 + 3HCl.$$

It is supposed that the enhanced activity of nascent hydrogen is due to the hydrogen in the atomic state which is exceptionally reactive. That is, hydrogen which is just liberated from a compound is in the state of free atoms and these atoms react before they have a chance to combine into molecules. Ordinary hydrogen consist of hydrogen molecules. Since atoms are more active than molecules, nascent hydrogen is more reactive than ordinary hydrogen.

But this theory of nascent hydrogen fails to explain the different reactivities of nascent hydrogen obtained from different sources. For example, nascent hydrogen obtained by the reaction of zinc on sulphuric acid can reduce potassium chlorate but the nascent hydrogen obtained by the reaction of sodium amalgam with water cannot reduce potassium chlorate. This is due to the reason that the nascent hydrogen becomes energised by acquiring energy evolved in a chemical reaction. Since different amount of energy is evolved in different reactions, nascent hydrogen obtained in different reactions has different energy. As a result, the reactivities of nascent hydrogen obtained from different sources become different.

Atomic hydrogen. At high temperatures the hydrogen molecule dissociates into atoms :

$$H_2 \rightleftharpoons H + H.$$

Atomic hydrogen is produced by heating tungsten wire electrically in an atmosphere of highly rarefied hydrogen. A large quantity of heat (about 102, 000 cal per gram molecule) are absorbed when hydrogen is decomposed into its atoms. Hence, atomic hydrogen must be much more reactive than molecular hydrogen.

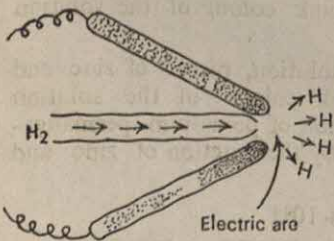


Fig. 1.10 : Change of molecular hydrogen into atomic hydrogen.

The atomic hydrogen is very short lived and recombines rapidly into molecules. When the atoms recombine they release the large quantity of energy which they absorbed during the decomposition of hydrogen molecules. Atomic hydrogen torches work on this principle. An electric arc is struck between two tungsten electodes and a jet of hydrogen from a cylinder is passed through the arc. Hydrogen molecules decompose into atoms which recombine into molecules at a short distance from the arc producing intensely hot flame. The high temperature of the flame is due to the energy released during the recombination of the atoms into molecules. The hot flame produced is capable of melting tungsten (m. pt. 3400°C). Atomic hydrogen flame is very suitable for welding metals.

Atomic hydrogen is very reactive and acts as a powerful reducing agent. It reduces oxides of certain metals and displaces silver, copper, mercury and lead from their salts. It combines with molecular oxygen to form hydrogen peroxide, reduces sulphur to hydrogen sulphide and combines with alkali metals to form their hydrides :

$$O_2+2H=H_2O_2\ ;\ S+2H=H_2S\ ;\ Na+H=NaH$$

It reacts with carbon monoxide to form formaldehyde :

$$CO+2H=HCHO.$$

Tests of hydrogen. (i) Hydrogen burns in oxygen or air with a pale blue flame. The only product of combustion is water which turns white anhydrous copper sulphate blue. (ii) Hydrogen is absorbed readily by palladium. The absorbed hydrogen is liberated again when palladium is heated.

Uses of hydrogen. Elemental hydrogen finds a number of large scale uses :

(i) It is used for filling balloons and air-ships. Nowadays hydrogen is replaced by helium for filling air-ships, since hydrogen is inflammable and hence its use is dangerous.

(ii) Large amounts of hydrogen are used in the synthesis of ammonia, hydrogen chloride and methanol, CH_3OH.

(iii) It is used in the recovery of certain metals from their oxides and chlorides.

(iv) Large amount of hydrogen are required in the hydrogenation of vegetable oils. Vegetable oils such as cotton-seed oil and coconut oil combine with hydrogen in the presence of a metal catalyst and are converted into fat substitutes that are used as food or are converted into soaps. It is also used for the hydrogenation of petroleum fractions and coal for producing synthetic petrol.

(v) It is used as a fuel in the oxyhydrogen and the atomic hydrogen torch which are used for fusing refractory metals for welding, for cutting and drilling metals.

Isotopes of hydrogen. Three isotopes of hydrogen are known : (i) ${}_1H^1$ — sometimes called protium but generally called hydrogen ; (ii) ${}_1H^2$ or D — called deuterium and (iii) ${}_1H^3$ or T — called tritium. All three isotopes are equal in atomic number and electric charge of their nuclei but differing in mass. The nucleus of protium is called *proton* consisting only of a proton, the nucleus of deuterium is called *deuteron* consisting of one proton and one neutron and the nucleus of tritium is called *triton* consisting of two neutrons and one proton. All of them contain one electron in the extranuclear shell. Owing to identical electronic configuration, chemical properties of the isotopes are largely the same. Since they differ in masses, their rates of reactions and equilibrium constants for corresponding reactions are different. For example, the rate of diffusion of protium is about $\sqrt{2}$ times that of deuterium. Due to differences in mass, a few detectable differences in physical properties, e.g., melting point, boiling point, etc., of protium and deuterium are observed. The differences of property which arise due to the difference in mass are called *isotopic effect.*

EXERCISE

1. How is hydrogen prepared in the laboratory? What are the precautions to be taken during the preparation? How is this gas purified?

2. State the physical and chemical properties of hydrogen.

3. With equations show four different methods for obtaining hydrogen gas from water. Which of the following metals would liberate hydrogen from cold water: Cu, Bi, Au. Pt, Mn, Na, Al?

4. Describe a method for the preparation of hydrogen by the interaction of a metal on acids. What metals are used and why? Why dilute and not concentrated sulphuric acid is used? Can nitric acid be used for preparing hydrogen? If not why?

5. Describe a method for the preparation of very pure hydrogen. What is nascent hydrogen? How would you prove that nascent hydrogen is a more powerful reducing agent than ordinary molecular hydrogen?
What do you mean by occlusion of hydrogen?

6. Describe kipp's generator with a neat sketch. Explain how a ready and controlled supply of hydrogen is obtained in the laboratory with the help of this apparatus.

7. Describe experiments to show that:

(a) Hydrogen burns in oxygen to form water.

(b) Hydrogen is a reducing agent and form water when it reduces an oxide.

(c) Hydrogen in the nascent state is more active than molecular hydrogen.

8. Describe a commercial method for the preparation of hydrogen. How is hydrogen separated from water gas?

9. Explain what happens when

(a) steam is passed over red-hot iron.

(b) hydrogen is passed over heated calcium and the product formed is treated with water.

(c) hydrogen is passed over heated copper oxide.

(d) aluminium shavings are boiled with 20% solution of caustic potash.

(e) zinc and dilute hydrochloric acid are added to ferric chloride solution.

(f) zinc and dilute sulphuric acid are added to potassium permanganate solution.

10. Write equations for the following reactions :

(a) Potassium+water.

(b) Mercuric oxide+hydrogen+heat.

(c) Zinc+strong solution of sodium hydroxide.

(d) Silicon+strong solution of caustic soda.

(e) Calcium hydride+water.

11. Explain the following statements :

(a) Commercial zinc and not pure zinc is used in the laboratory preparation of hydrogen from dil. H_2SO_4 or dil. HCl.

(b) Nitric acid is not used in the preparation of hydrogen.

(c) Conc. H_2SO_4 is not used in the preparation of hydrogen by the action of zinc.

(d) Atomic hydrogen enters into reactions of which the molecular hydrogen is quite incapable under the same conditions.

(e) Copper cannot liberate hydrogen from dilute acids.

(f) In water, proton (hydrogen cation) exists as hydronium ion.

12. Write notes on : (a) atomic hydrogen, (b) nascent hydrogen and (c) atomic hydrogen torch.

13. Explain the principle upon which atomic hydrogen welding is based.

14. Discuss the role of metallic impurities in the preparation of hydrogen from dil. acid by the action of zinc.

CHAPTER II

OXYGEN AND OZONE

Joseph Priestley, an English chemist, discovered oxygen in 1774. He prepared it by heating some red mercuric oxide which was confined over mercury into the top of a closed tube which had been filled with mercury ; its open lower end being under the surface of a bath of mercury. The mercuric oxide was heated by the concentration of the sun's rays over it by means of a lens. The reaction was $2HgO=2Hg+O_2$. K. W. Scheele of Sweden prepared and investigated oxygen before 1773, but since he did not publish an account of his work until 1777, he is not given priority credit. In 1775, Lavoisier, having learned about Priestley's work took up the study of the properties of oxygen. He established that the gas was a component part of air. He gave it the name oxygen (Greek, *oxys*, acids and *geon*, to form) because he thought mistakably that it was essentia constituent of all acids.

Of all the elements found on the earth, oxygen is most abundunt. In the free state, it occurs in the atmospheric air and constitutes 23·2% by weight or 20·9% by volume of the atmosphere. In the combined state, oxygen occurs in water, in nearly all rocks, in many minerals, in all plants and animals. Combined with hydrogen in water it constitutes about 86% by weight of the oceans which cover the earth. Minerals such as sand, SiO_2, limestone $CaCO_3$ and clay contain large quantity of oxygen. Oxygen constitutes about 50% of the earth's crust.

Preparation. Oxygen can be prepared from (1) air ; (2) water and (3) compounds of oxygen.

(1) **From air.** Since approximately 20% of air consists of oxygen, air is the primary source of oxygen. There are two methods which are readily applicable to the preparation of oxygen, viz., (i) Brin's process, and (ii) Fractional distillation of liquid air.

(i) **Brin's process.** If baryta (barium oxide, BaO) is heated at a temperature of 500°C in air at atmospheric pressure, barium peroxide is formed. Barium peroxide thus formed when heated to 700°C, decomposes to yield oxygen and barium oxide again.

$$2BaO+O_2 \overset{500°C}{=} 2BaO_2$$

$$2BaO_2 \overset{700°C}{\rightleftharpoons} 2BaO+O_2$$

Such a process which involves a series of reactions that lead back to the starting materials is called a cyclic process. Only air and heat are necessary for the successful operation of this process.

(ii) **Fractional distillation of liquid air.** Air is first liquefied. The liquid air is a mixture of liquid nitrogen (b. pt. —195·8°C) and liquid oxygen (b. pt., —183°C). So when the liquid air is distilled, nitrogen which is more volatile, boils off first, leaving oxygen as a residue. Pure liquid oxygen has a pale blue colour.

(2) **From water.** Oxygen can be prepared conveniently from water by the following processes :

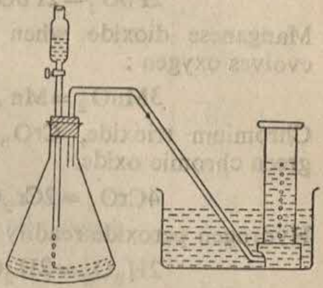


Fig. 2.1 : Preparation of oxygen at ordinary temperature.

(i) **Action of sodium peroxide on water.** Solid sodium peroxide is taken into a conical flask fitted with a dropping funnel and a delivery tube. Water is then added on to sodium peroxide drop by drop from the dropping funnel. Sodium peroxide reacts immediately with water at room temperature. Oxygen which is evolved during the reaction is then collected by the displacement of water (fig. 2.1).

$$2Na_2O_2+2H_2O=4NaOH+O_2$$

Sodium hydroxide is soluble in water and remains dissolved.

(ii) **Electrolysis of water.** When acidulated water is electrolysed, oxygen is liberated at the positive electrode. Electrolysis of a solution of bariam hydroxide with nickel electrodes also liberates oxygen.

(iii) **Action of chlorine on steam.** A mixture of steam and chlorine is passed through a strongly heated silica tube containing pieces of broken porcelain. Chlorine combines with hydrogen of steam to form hydrogen chloride and oxygen is set free :

$$2H_2O+2Cl_2=4HCl+O_2$$

Oxygen is freed from hydrogen chloride by passing the mixture through a caustic soda solution in a wash-bottle which absorbs hydrogen chloride only. Oxygen is then collected by the displacement of water.

(3) **From compounds of oxygen.** (i) **By heating oxides of metals.** Oxygen may be obtained by heating certain metallic oxides such as those of mercury, silver, gold and platinum. When mercuric oxide is heated strongly in a hard-glass tube, globules of mercury collect in the cooler parts of the tube and oxygen gas is evolved. Oxygen may be collected over mercury.

$$2HgO=2Hg+O_2$$

Silver oxide when heated decomposes at a lower temperature and gives good yields of oxygen.

$$2Ag_2O=4Ag+O_2$$

Oxygen can be prepared by heating certain higher oxides of metals. A lower oxide of the metal is formed. Red lead, Pb_3O_4, when heated evolves oxygen and leaves a lower oxide of lead called litharge :

$$2Pb_3O_4=6PbO+O_2$$

Lead dioxide also gives oxygen when heated.

$$2PbO_2 = 2PbO + O_2$$

Manganese dioxide when heated gives trimanganic tetroxide and evolves oxygen :

$$3MnO_2 = Mn_3O_4 + O_2$$

Chromium trioxide, CrO_3, evolves oxygen when heated, leaving green chromic oxide.

$$4CrO_3 = 2Cr_2O_3 + 3O_2$$

Hydrogen peroxide readily loses oxygen to form water.

$$2H_2O_2 = 2H_2O + O_2$$

(ii) **From oxy-acids and oxy-salts.** (a) **From nitric acid or sulphuric acid.** When concentrated sulphuric acid or nitric acid is allowed to fall drop by drop on pumice stone heated to bright redness, oxygen, water and sulphur dioxide or nitrogen dioxide are formed.

$$2H_2SO_4 = 2SO_2 + 2H_2O + O_2$$
$$4HNO_3 = 4NO_2 + 2H_2O + O_2$$

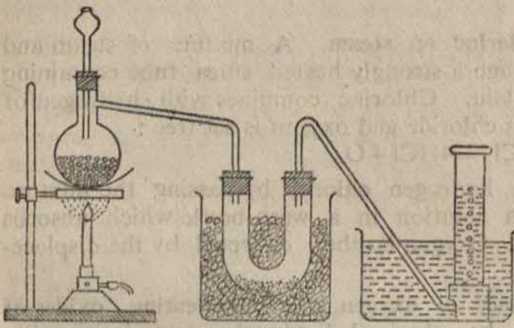


Fig. 2.2 : Preparation of oxygen from conc. H_2SO_4 or conc. HNO_3.

Some pumice stones are taken into a distilling flask fitted with a dropping funnel. The flask is strongly heated and conc. H_2SO_4 or conc. HNO_3 is allowed to fall drop by drop on the pumice stone. A mixture of oxygen and sulphur dioxide or nitrogen dioxide is formed ; the mixture is then allowed to pass through a U-tube kept immersed in a freezing mixture. SO_2 or NO_2 condenses to a liquid in the U-tube but oxygen passess out and is collected over water.

(b) **From metallic nitrates.** Most of the metallic nitrates evolve oxygen when heated. The formation of the other product depends on the activity of the metals. From this view point, metals are divided into three classes (fig. 2·3).

(i) Sodium nitrate and potassium nitrate (class A in the figure 2·3) when heated give off oxygen and leave sodium nitrite and potassium nitrite respectively.

$$2NaNO_3 = 2NaNO_2 + O_2$$
$$2KNO_3 = 2KNO_2 + O_2$$

(ii) The nitrates of the metals of class B when heated decompose into the oxide of the metal, nitrogen di-oxide and oxygen.

$$2Ba(NO_3)_2 = 2BaO + 4NO_2 + O_2$$
$$2Ca(NO_3)_2 = 2CaO + 4NO_2 + O_2$$
$$2Zn(NO_3)_2 = 2ZnO + 4NO_2 + O_2$$
$$2Cu(NO_3)_2 = 2CuO + 4NO_2 + O_2$$
$$2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2$$

(iii) The nitrates of the metal of class C decompose into metal, nitrogen di-oxide and oxygen.

$$Hg(NO_3)_2 = Hg + 2NO_2 + O_2$$
$$2AgNO_3 = 2Ag + 2NO_2 + O_2$$

Ammonium nitrate is exceptional ; it decomposes into nitrous oxide and water :

$$NH_4NO_3 = N_2O + 2H_2O$$

Some lead nitrate are taken into a hard-glass test tube which is connected to a U-tube kept immersed in a freezing mixture (fig. 2.4). The test tube is then strongly heated when a mixture of nitrogen dioxide and oxygen is formed ; the mixture passes through the U-tube where nitrogen dioxide condenses to a liquid. Oxygen passes out and collects over water in a gas-jar.

K Na	A
Ba Sr Ca Mg Al Zn Fe Sn Pb Cu	B
Hg Ag Au Pt	C

Fig. 2.3

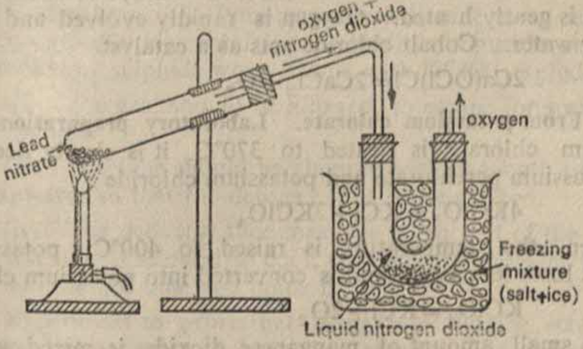


Fig. 2.4 : Preparation of oxygen by thermal decomposition of lead nitrate.

(c) Potassium dichromate and potassium permanganate when strongly heated evolves oxygen.

$$4K_2Cr_2O_7 = 4K_2CrO_4 + 2Cr_2O_3 + 3O_2$$
$$2KMnO_4 = K_2MnO_4 + MnO_2 + O_2$$

Potassium permanganate reacts with warm dilute sulphuric acid to evolve oxygen.

$$4KMnO_4+6H_2SO_4=2K_2SO_4+4MnSO_4+6H_2O+5O_2$$

When heated with conc. H_2SO_4, $KMnO_4$ explodes violently. Potassium dichromate evolves oxygen when heated with conc. H_2SO_4.

$$2K_2Cr_2O_7+10H_2SO_4=4KHSO_4+2Cr_2(SO_4)_3+8H_2O+3O_2$$

(d) When hydrogen peroxide solution is mixed with a solution of potassium permanganate and dilute sulphuric acid, oxygen is evolved. Oxygen thus obtained is pure.

$$2KMnO_4+3H_2SO_4+5H_2O_2=K_2SO_4+2MnSO_4+8H_2O+5O_2$$

In this reaction, potassium permanganate and hydrogen peroxide mutually decompose each other. By this process oxygen is prepared at ordinary temperature, i.e., without the application of heat to the reacting substances.

A solution of hydrogen peroxide is taken into a conical flask fitted with a dropping funnel and a delivery tube (fig. 2.1). The free end of the delivery tube is introduced into a gas-jar filled with water and kept inverted into water in a trough. A cooled mixture of potassium permanganate solution and dilute sulphuric acid is taken in the dropping funnel and allowed to fall drop by drop into hydrogen peroxide solution. The oxygen evolved is collected over water.

(e) **From bleaching powder.** A solution or paste of bleaching powder to which have been added a few drops of cobalt chloride solution is gently heated. Oxygen is rapidly evolved and is collected over water. Cobalt chloride acts as a catalyst.

$$2Ca(OCl)Cl=2CaCl_2+O_2$$

(f) **From potassium chlorate. Laboratory preparation.** When potassium chlorate is heated to 370°C. it is slowly decomposed into potassium perchlorate and potassium chloride :

$$4KClO_3=KCl+3KClO_4$$

When the temperature is raised to 400°C, potassium perchlorate loses its oxygen and is converted into potassium chloride :

$$KClO_4=KCl+2O_2$$

If a small amount of manganese dioxide is mixed with potassium chlorate, the reaction proceeds readily at a much lower temperature. In the laboratory, therefore, oxygen is prepared by heating a mixture of potassium chlorate and manganese dioxide. Manganese dioxide acts as a catalyst. Only potassium chlorate is decomposed and in this case, there is no formation of potassium perchlorate.

$$2KClO_3+[MnO_2]=2KCl+3O_2+[MnO_2]$$

Potassium chlorate is mixed with $\frac{1}{5}$ of its weight of manganese dioxide and the mixture is taken in a hard-glass test tube. The test tube is fitted with a cork through which passes a delivery tube and is clamped in a horizontal position with its cork-end inclined slightly downwards. The end of the delivery tube is introduced into a gas-jar full of water which is kept inverted on a beehive shelf in a trough (fig. 2.5). The test tube is now heated cautiously with a small flame. Oxygen which is evolved, passes through the delivery tube and collects inside the gas-jar by the displacement of water.

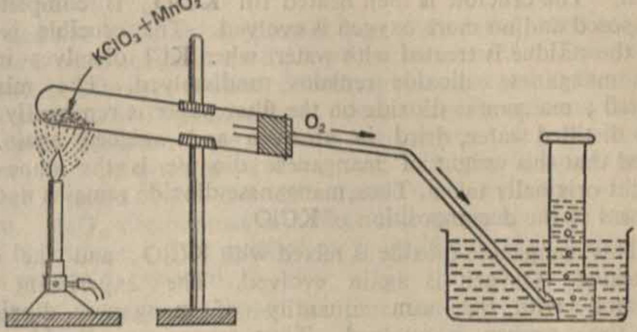


Fig. 2.5 : Laboratory method of preparation of oxygen.

Precautions. (i) Pure manganese dioxide must be used, because manganese dioxide containing combustible impurities such as charcoal or antimony sulphide when heated with $KClO_3$ explodes violently.

(ii) The gas should be allowed to escape for some time before collection.

(iii) The tube should be clamped with its mouth slightly inclined downwards so that the delivery tube is not choked.

(iv) The delivery tube must be taken out of the water before the test tube is allowed to cool, since otherwise water will be sucked up into the hot tube and crack it.

Experiment to prove that manganese dioxide acts as a catalyst in the decomposition of potassium chlorate. In order to prove the catalytic activity of manganese dioxide, we must prove that (i) it increases the rate of decomposition of $KClO_3$ and (ii) it remains unchanged in mass and chemical composition after the reaction.

(i) Potassium chlorate is taken in one test tube and a mixture of potassium chlorate and manganese dioxide (in the ratio 5 : 1) is taken in another test tube. The two test tubes are embedded in a sand-tray and heated. It is found that oxygen is first evolved from the tube which contains the mixture. Hence, manganese dioxide accelerates the rate of decomposition of potassium chlorate.

(ii) A porcelain crucible containing about 5 grams of potassium chlorate is weighed accurately. Then about 1 gram of manganese dioxide is added to it and again weighed. The difference in the two weights gives the weight of manganese dioxide taken. The crucible is then heated till $KClO_3$ is completely decomposed and no more oxygen is evolved. The crucible is cooled and the residue is treated with water when KCl dissolves in water but manganese dioxide remains undissolved. The mixture is filtered ; manganese dioxide on the filter paper is repeatedly washed with distilled water, dried in air-oven and weighed again. It is found that this weight of manganese dioxide is the same as the weight originally taken. Thus, manganese dioxide remains unchanged in mass in the decomposition of $KClO_3$.

This manganese dioxide is mixed with $KClO_3$ and the mixture is heated. Oxygen is again evolved. The experiment can be repeated with the same quantity of manganese dioxide and each time oxygen is evolved. Thus, manganese dioxide remains unchanged in chemical composition during the decomposition of potassium chlorate.

Experiment to prove that the residue left in the tube is a chloride and not a chlorate. The filtrate obtained when the water extract of the residue in the crucible (in experiment ii) is filtered, is treated with silver nitrate solution when a curdy white precipitate is formed. The precipitate is insoluble in nitric acid, but soluble in ammonium hydroxide. On adding silver nitrate solution to a solution of $KClO_3$, no such precipitate is obtained. Hence, the residue left in the crucible when $KClO_3$ is heated with MnO_2 must be a chloride.

$$KCl + AgNO_3 = KNO_3 + AgCl$$

Preparation of pure oxygen. (i) Pure oxygen can be prepared by the electrolysis of a warm solution of barium hydroxide in water, using nickel electrodes.

(ii) Pure oxygen is best prepared by the reaction of hydrogen peroxide with acidified potassium permanganate solution. Oxygen is dried by means of phosphorus pentoxide and is collected over mercury.

(iii) Potassium permanganate solution in water is acidified with sulphuric acid and boiled in order to free it from dissolved gases. On electrolysis of this solution, very pure oxygen is liberated at the anode. The gas is passed through a U-tube containing phosphorus pentoxide and is collected over mercury.

Industrial preparation. Oxygen is prepared on a large scale (a) by Brin's process ; (b) by fractional distillation of liquid air and (c) by electrolysis.

(a) **Brin's process.** This method is based on the fact that barium oxide, BaO, when heated in procelain tubes to 500°C in current of air forms barium peroxide BaO_2 and at a temperature of 800°C, this is again split up into barium oxide and oxygen. On lowering the temperature again, the regenerated barium oxide absorbs further oxygen from the air with the formation of the peroxide. Thus, the same quantity of barium oxide can be used again and again.

Purified and dried air is passed into cylindrical, vertical cast iron retorts which contain hard porous barium oxide. The retorts are heated in a furnace to about 550°C and air is kept into the retorts under a pressure of 1½ atmospheres. Under these conditions, barium oxide rapidly absorbs oxygen to form barium peroxide ; unabsorbed nitrogen passes off ; the air is then shut off ; the temperature of the retort is raised to 700°C and the retort is evacuated to a lower pressure. BaO_2 decomposes into BaO and oxygen. The evolved oxygen is removed. The purified air is again passed into the retort and the process is repeated.

In practice many difficulties are encountered and the process is now obsolete.

(b) **Fractional distillation of liquid air.** Oxygen is nowadays obtained on a large scale from liquid air. Liquid air is manufactured by a method invented by Hampson and Linde. This method is based upon the fact that when a gas under high pressure is allowed to expand through a small orifice, the gas is cooled down. The machine in which air is liquefied is described below :

Air is first purified from dust, carbon dioxide and water vapour and the purified air is allowed to pass through a tube and is compressed to about 200 atmospheres by pump X. The compressed air is now allowed to flow through pipes Y cooled by running cold water and the heat, which is produced during compression is absorbed. The cold, high pressure gas then enters the liquefier Z through the inner pipe L of the two concentric metal pipes wound in the form of a spiral. At the end of the inner tube, there is a small orifice O through which the air expands to a lower pressure in chamber M. The air is cooled as a result of this expansion. The cold air now passes up the outer tube, Q and is again compressed. The compressed air passes down the inner pipe and is cooled by the gas

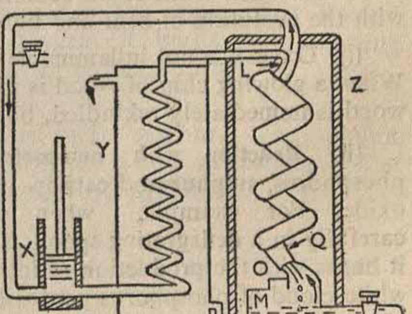


Fig. 2.6

passing upwards through the outer pipe. The cold compressed gas is again allowed to expand through the orifice and consequently becomes still colder. This process is repeated until the air liquefies.

The liquid air is then distilled in a fractionating column, when the more volatile nitrogen first distils off and escapes and almost pure liquid oxygen is left at the bottom of the fractionating column.

The liquid oxygen is now vapourised and stored in steel cylinders at pressure of about 2000 lb/inch^2.

Liquid oxygen can be kept for appreciable periods of time in a double walled flask called Dewar flask. The inside walls of the flask are silvered and the space between the walls is evacuated. Common thermosflask is similar to the Dewar flask.

Properties (a) **Physical properties.** Ordinary oxygen exists as a diatomic molecule, O_2. It is a colourless, odourless and tasteless gas and is slightly heavier than air. Oxygen is slightly soluble in water ; the dissolved oxygen in water serves for the respiration of aquatic animals.

When cooled to — 183°C at atmospheric pressure, it condenses to a pale blue liquid. On further cooling the liquid freezes at —218·4°C to a pale blue crystalline solid. The liquid and solid oxygen are highly magnetic.

(b) **Chemical properties.** Oxygen is a very active element which reacts with most elements and compounds. The reactions usually occur slowly at ordinary temperature, but take place quite rapidly when heated.

Combustion is the rapid combination of oxygen with substances with the evolution of heat and light.

(i) Oxygen is not inflammable but is a supporter of combustion. When a glowing chip of wood is introduced in a jar of oxygen, the wood is immediately rekindled, but oxygen does not burn.

(ii) **Reaction with non-metals.** Some non-metals such as phosphorus, sulphur and carbon reacts with oxygen to form acidic oxide. For example, when white phosphorus after heating carefully in a deflagrating spoon, is plunged into a jar of oxygen, it burns with the production of intense heat and light, forming dense white cloud of phosphorus pentoxide.

$$4P+5O_2 = 2P_2O_5$$

Phosphorus pentoxide when treated with water, forms phosphoric acid.

$$P_2O_5+3H_2O=2H_3PO_4$$

Feebly burning sulphur when thrust into oxygen, burns more vigorously forming sulphur dioxide. A little sulphur trioxide is also formed.

$$S+O_2 = SO_2$$
$$2S+3O_2 = 2SO_3$$

When shaken with water, the product of combustion dissolves forming solution which is acidic to litmus.

$$SO_2+H_2O=H_2SO_3 \qquad SO_3+H_2O=H_2SO_4$$

Finely divided charcoal (carbon) is first heated in a spoon. The heated charcoal is then poured into a jar of oxygen, when it burns brilliantly, often throwing off bright sparks. The product of the reaction is carbon dioxide. $C+O_2=CO_2$

Carbon dioxide dissolves in water, forming a weak unstable acid :

$$CO_2+H_2O=H_2CO_3$$

(iii) **Reaction with metals.** Almost all metals except silver, gold and platinum metals, react with oxygen when heated, forming oxides of the metals.

The alkali and alkaline earth metals react most readily with oxygen. When sodium and potassium after heating in iron deflagrating spoon are thrust into a jar of dry oxygen, they burn with bright yellow and violet flames respectively, forming mainly peroxides

$$2Na+O_2=Na_2O_2$$
$$2K+O_2=K_2O_2$$

The products of the reaction when dissolved in water form solutions which are alkaline to litmus paper and contain sodium hydroxide and potassium hydroxide :

$$2Na_2O_2+2H_2O=4NaOH+O_2$$
$$2K_2O_2+2H_2O=4KOH+O_2$$

When a magnesium ribbon is heated in the flame of a Bunsen burner and inserted into a jar of oxygen, it burns with dazzling brilliancy, forming magnesium oxide or magnesia, MgO :

$$2Mg+O_2=2MgO$$

The end of an iron wire is coated with sulphur. The sulphur is ignited and the wire is then inserted into a jar of oxygen. The metal burns with brilliancy, forming ferrosoferric oxide.

$$3Fe+2O_2=Fe_3O_4$$

The same reaction takes place when red-hot iron is immersed in pure oxygen.

(iv) **Reaction with compounds.** Some of the familiar and common reactions of oxygen with compounds are described below :

(a) Oxygen reacts with nitric oxide in the cold to give brown fumes of nitrogen dioxide :

$$2NO+O_2=2NO_2$$

(b) Oxygen oxidises sulphurous acid, ferrous salts and stannous salts in the cold, as shown by the equations :

$$2H_2SO_3 + O_2 = 2H_2SO_4$$
$$4FeSO_4 + 2H_2SO_4 + O_2 = 2Fe_2(SO_4)_3 + 2H_2O$$
$$2SnCl_2 + 4HCl + O_2 = 2SnCl_4 + 2H_2O$$

(c) Acetylene burns in oxygen to form carbon dioxide and water :

$$2C_2H_2 + 5O_2 = 4CO_2 + 2H_2O$$

Similiarly, methane burns in excess of oxygen to form CO_2 and water :

$$CH_4 + 2O_2 = CO_2 + 2H_2O$$

Ethyl alcohol is oxidised by oxygen to form CO_2 and water :

$$2C_2H_5OH + 6O_2 = 4CO_2 + 6H_2O$$

(d) An acid solution of chromous chloride is oxidised by oxygen with the formation of chromic chloride. The solution turns from blue to green :

$$4CrCl_2 + 4HCl + O_2 = 4CrCl_3 + 2H_2O$$

Tests. (i) Oxygen rekindles a glowing chip of wood.

(ii) Oxygen produces brown fumes of nitrogen dioxide with nitric oxide.

Absorbents. (i) Oxygen is absorbed by (i) alkaline pyrogallate solution ; (ii) ammonical cuprous chloride solution which turns deep blue ; (iii) acid solution of chromous chloride which turns from blue to green.

Uses. Oxygen is one of the most useful elements. (i) It plays an exceedingly important part in nature. It is usually indispensable for respiration, one of the most important vital processes.

(ii) Oxygen is used in oxyacetylene and oxyhydrogen torches which are used in the welding and cutting of steels and other metals.

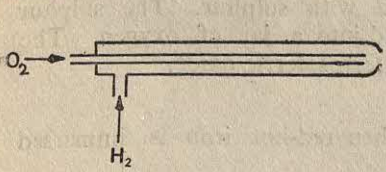


Fig. 2.7 : Oxy-hydrogen torch.

Fig. 2·7 shows an oxyhydrogen torch consisting of two concentric tubes. Oxygen is supplied to the inner and hydrogen to the outer tube of the torch. When the mixture of the two gases are lighted at the jet, a blue, pointed and intensely hot flame is produced.

In oxyacetylene flame, acetylence gas is used in place of hydrogen. The oxyacetylene torch reaching 3300°C is used extensively for welding.

If oxyhydrogen flame impinges on a stick of lime, lime becomes incandescent and glows with intensely white light called lime light.

(iii) Liquid oxygen is also used to burn fuel in some types of large rockets.

(iv) Oxygen is used in many industrial processes. For example, it is used in roasting of ores, in oxidation of sulphur for the manufacture of sulphuric acid, and in the oxidation of ammonia for the manufacture of nitric acid.

OZONE

In 1875, Van Marum, a Dutch chemist, noticed that the air in the vicinity of an electrical machine in motion produced a peculiar smell. Schönbein, in 1840, first recognised that this odour is due to the formation of a new gas to which he gave the name *ozone*. (Greek, ozo=I smell).

Ozone is present in small quantities in sea air. It is produced in the neighbourhood of water-falls. Ozone is formed in the upper layers of the atmosphere by the action of ultraviolet light from the sun on the oxygen. During thunderstorms, appreciable quantity of ozone is produced in the atmosphere. It is produced during the working of electrical machine.

Preparation. Ozone is prepared by passing oxygen or air through an electric discharge. Oxygen is partially converted into ozone.

$$3O_2 \rightleftharpoons 2O_3 - 68{,}000 \text{ calories}$$

The reaction is endothermic. The formation of ozone is, therefore, favoured at high temperatures. At ordinary temperatures, however, ozone tends to decompose completely and hence after the formation of ozone at high temperatures, it must be rapidly cooled in order to retain it.

Again, heat generated by ordinary electrical discharge would decompose most of the ozone as soon as it is formed and, therefore, a high voltage low temperature electrical discharge or silent electrical discharge is used. If layers of an insulating material such as glass are placed in the gap through which the discharge is passed, a vast number of minute sparks are obtained. As a result, there is no local elevation of temperature and these minute sparks are better agents for producing ozone than a heavier discharge.

Oxygen must be pure and dry and must be maintained at low temperatures in order to get the good yield of ozone, but even so only part of oxygen is converted into ozone. The apparatus which is used for converting oxygen into ozone is called an ozoniser.

In the laboratory, ozone is prepared by using two types of ozoniser—(i) Siemen's ozoniser and (ii) Brodie's ozoniser.

(i) **Siemen's ozoniser.** It consists of two concentric glass tubes. The inner surface of the inner tube and the outer surface of the outer tube are coated with tin foils. The sheets of tin foil are connected to the terminals of an induction coil, and a current of dry and pure oxygen is slowly passed through the annular space between the concentric tubes. Oxygen is thus subjected to the silent electric discharge which passes between the sheets of tin foils separated by the glass of the tubes. Oxygen is partially converted into ozone and the gas coming out of the tube contains 3 to 8 per cent of ozone.

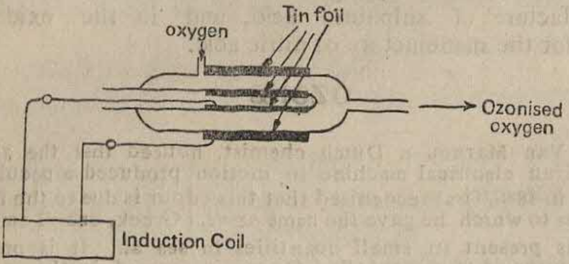


Fig. 2.8 : Siemen's ozoniser.

(ii) **Brodie's ozoniser.** It consists of two concentric glass tubes. The inner tube is closed at the bottom and is fitted into the outer tube with a ground glass joint. The outer tube is provided with an inlet tube through which oxygen is passed into the apparatus and with an outlet tube through which the ozonised gas escapes (fig. 2.9). The inner tube is filled with dilute sulphuric acid solution and the entire apparatus is kept immersed in a beaker containing the same solution. The wires from an induction coil are dipped into the two solutions. Thus, the solutions are electrodes and at the same time serve to cool the gas. A slow stream of pure and dry oxygen is passed through the annular space between two glass tubes and the induction coil is set to work. Oxygen is thus subjected to a silent electric discharge which occurs in the space between the tube walls. Oxygen coming out of the ozoniser contains several per cent of ozone. The lower is the temperature, the more ozone is formed.

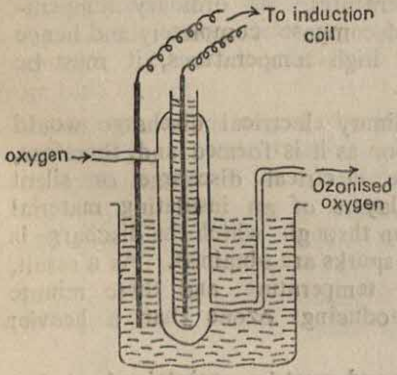


Fig. 2.9 : Brodie's ozoniser.

Preparation of pure ozone. Oxygen mixed with ozone coming out of the ozoniser is passed through a tube cooled in liquid air, when a blue liquid is obtained. This blue liquid is a solution of ozone in liquid oxygen. Fractional distillation of this liquid gives pure liquid ozone which is dark blue in colour and boils at −112°C. On careful evaporation of pure liquid ozone, pale blue pure gaseous ozone is obtained.

Other methods of formation of ozone. Ozone can also be prepared by the following methods :

(i) Ozone is formed when an ice-cold dilute sulphuric acid solution is electrolysed, using a high current density. The gas which is liberated at the platinum anode contains about 14 per cent of ozone.

(ii) Small quantities of ozone are produced when fluorine reacts with water at 0°C.

(iii) It is formed by slow oxidation in a large bottle containing moistened phosphorus, partly immersed in water.

(iv) Ozonised oxygen is also obtained by the action of sulphuric acid on barium peroxide, BaO_2 or potassium parmanganate.

$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O + \text{(ozonised oxygen)}.$$

(v) Ozonised oxygen is produced when hot platinum wire is plunged into liquid oxygen.

(vi) It is also formed by the action of ultra-violet rays and radium emanations on oxygen.

Properties. (A) **Physical properties.** (i) Ozone is a pale blue gas with bad fishy smell and exists as a triatomic molecule. It is heavier than oxygen and air. It is slightly soluble in water but more soluble than oxygen. It is readily soluble in certain essential oils such as turpentine, cinnamon oil, etc.

(ii) When cooled to −112°C ozone condenses into a deep blue liquid which is highly explosive and magnetic. By strong cooling and evaporating under low pressure black crystals of solid ozone are obtained.

(iii) At ordinary temperature, ozone is quite stable but decomposes rapidly when heated. The decomposition is greatly accelerated by certain substances such as platinum black, dust particles, silver oxide, manganese dioxide, etc., all of which act as positive catalysts. On the other hand, water acts as a negative catalyst, i.e., it stabilises ozone. The decomposition of ozone is accompanied by evolution of heat and an increase in volume of one and a half times since every two ozone molecules turn into three molecules of oxygen :

$$2O_3 = 3O_2 + 68{,}000 \text{ calories}$$

(B) Chemical properties. Since the decomposition of ozone into oxygen is exothermic, ozone is a much more energetic substance than oxygen. Hence, it is much more reactive than oxygen. Many substances which do not react or react with oxygen at elevated temperature only, readily react with ozone at ordinary temperature.

(1) **Oxidising property.** Ozone is a very powerful oxidising agent. The following are the examples in which ozone acts as oxidising agent.

(a) Oxidation of metals. It oxidises most of the metals with the exception of gold and platinum. Under the action of ozone, a shining silver plate blackens rapidly, being covered with a layer of silver oxide Ag_2O

$$2Ag+O_3=Ag_2O+O_2$$

When ozone is passed into a flask containing a little mercury, mercury loses its lustre and spreads as a film over the walls of the flask. This action is due to the oxidation of mercury to mercurous oxide.

$$2Hg+O_3=Hg_2O+O_2$$

On shaking with water, the mercury recovers its original form.

(b) Oxidation of non-metals. Dry yellow and red phosphorus are oxidised to phosphorus pentoxide by ozone. If water is present phosphoric acid is formed.

$$2P+3O_3=P_2O_5+2O_2$$

$$P_2O_5+3H_2O=2H_3PO_4$$

Similiarly, arsenic in presence of water is oxidised by ozone to arsenic acid.

Dry sulphur is oxidised to sulphur trioxide ; if sulphur is moist, then sulphuric acid is formed. Dry iodine is converted into a yellow powder I_4O_9 but moist iodine is oxidised to iodic acid by ozone.

$$2I_2+9O_3=I_4O_9+9O_2$$

$$I_2+5O_3+H_2O=2HIO_3+5O_2$$

(c) Oxidation of compounds. (i) Ozone oxidises lead sulphide to lead sulphate and ferrous salts to ferric salts :

$$PbS+4O_3=PbSO_4+4O_2$$

$$2FeSO_4+H_2SO_4+O_3=Fe_2(SO_4)_3+H_2O+O_2$$

Ozone oxidises hydrogen sulphide to sulphuric acid :

$$H_2S+4O_3 = H_2SO_4 +4O_2$$

Ozone liberates iodine from a neutral solution of potassium iodide. The solution becomes alkaline after the reaction :

$$2KI+H_2O+O_3=I_2+2KOH+O_2$$

Iodine is also liberated by ozone from acidified solution of potassium iodide :

$$2KI+2HCl+O_3=2KCl+I_2+O_2+H_2O$$

If a piece of paper moistened with a solution of potassium iodide and starch solution is brought into contact with air containing ozone, the paper immediately turns blue owing to the liberation of iodine.

Sodium nitrite solution is oxidised to sodium nitrate by ozone :

$$NaNO_2+O_3=NaNO_3+O_2$$

Ozone liberates halogens from their hydracids.

$$2HX+O_3=X_2+H_2O+O_2 \quad (X=Cl, Br, \text{ and } I)$$
$$2HCl+O_3=Cl_2+H_2O+O_2$$

Ozone reacts with hydriodic acid liberating iodine and forming hydrogen peroxide. The hydrogen peroxide is formed possibly by the side reaction. The reaction is represented by the following equations :

$$2HI+O_3=I_2+H_2O+O_2$$
$$4HI+O_3=2I_2+H_2O+H_2O_2$$

In these reactions, it appears that ozone first breaks down into a molecule of oxygen and free atom of oxygen :

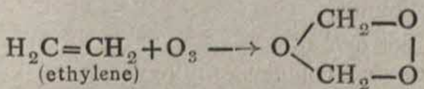
$$O_3=O_2+O$$

It is this atomic oxygen which oxidises the compounds.

(ii) There are certain reactions in which the whole of the oxygen in the ozone molecule is used up and no oxygen is set free, e.g., in the oxidation of sulphur dioxide to sulphur trioxide and of stannous chloride to stannic chloride.

$$3SO_2+O_3=3SO_3$$
$$3SnCl_2+6HCl+O_3=3SnCl_4+3H_2O$$

Ozone adds to unsaturated organic compounds, e.g., ethylene, benzene, etc., to form unstable addition compounds which are known as ozonides :



(ethylene ozonide)

$$C_6H_6+3O_3 = \underset{\text{(benzene ozonide)}}{C_6H_6(O_3)_3}$$

Ozone destroys rubber since it contains unsaturated organic compound.

(2) **Reducing property.** Ozone reduces a few compounds such as barium peroxide, BaO_2, hydrogen peroxide, H_2O_2, etc., but it has no action on potassium permanganate or potassium dichromate.

$$BaO_2 + O_3 = BaO + 2O_2$$
$$H_2O_2 + O_3 = H_2O + 2O_2$$

Ozone reduces silver oxide to silver and lead di-oxide to lead monoxide.

$$Ag_2O + O_3 = 2Ag + 2O_2 \;;\; PbO_2 + O_3 = PbO + 2O_2$$

In these reactions, ozone is not oxidised but it is also reduced. Hence, these are not oxidation-reduction reactions.

(3) **Bleaching property.** Ozone bleaches indigo solution and vegetable colours. It bleaches oils, waxes, flour, starch and ivory. The bleaching property of the ozone depends on its oxidising ability.

$$O_3 = O_2 + [O]$$

$$[O] + \text{coloured substance} = \text{oxidised colourless substance}$$

Tests. Ozone is characterised by the following tests :

(i) It has a characteristic fishy smell. (ii) when a globule of mercury is shaken with ozone, mercury loses its lustre and spreads as a film on the walls of the flask ; (iii) it turns starch-iodide paper blue ; (iv) it turns filter paper soaked with alcoholic solutions of tetramethyl base violet—the paper is unaffected by hydrogen peroxide ; (v) it turns filter paper soaked with alcoholic solution of benzidine brown—this paper remains unaffected by hydrogen peroxide ; (vi) ozone cannot decolourise acidulated potassium permanganate solution.

Absorbents. Ozone is readily absorbed by (i) oil of cinnamon and (ii) oil of turpentine.

Uses. (i) Ozone kills bacteria by oxidation and hence it is used to disinfect water and air.

(ii) It is used as a bleaching agent.

(iii) A fuel system of ozone and cyanogen C_2N_2 gives a higher combustion temperature than any other rocket propellant system.

(iv) It is used as an oxidizing agent—for oxidising many organic and inorganic compounds.

Ozone is an allotrope of oxygen. The following experiments serve to show that ozone contains only oxygen. Very pure and dry oxygen is taken in a sealed tube attached to a manometer. Oxygen is then subjected to silent electric discharge in the tube when a contraction of volume is observed. On heating the ozonised oxygen so formed in the tube to 300°C, expansion to the original volume takes place. Hence, ozone is a form of oxygen.

This conclusion is further confirmed as follows : Pure and dry oxygen is subjected to a silent electric discharge in a tube and a piece of starch iodide paper is held into the gas when it turns blue, showing that ozone has been formed in the tube. Now the tube is heated to about 300°C and a piece of starch iodide paper is held into the gas. The paper is not turned blue, showing that ozone has been completely decomposed. Again, a few drops of alkaline pyrogallate solution are added into the tube. The tube is shaken well and inverted into water in a jar. Water rises up and completely fills the tube. Since only oxygen is absorbed by alkaline pyrogallate solution, oxygen is the only product in the decomposition of ozone. Hence, ozone contains atoms of oxygen only, and, therefore, is an allotrope of oxygen.

APPENDIX

Comparative study of oxygen and ozone.

Oxygen	Ozone
Colourless, odourless gas.	Pale blue gas having fishy smell.
Vapour density (H = 1) is 16.	Vapour density (H = 1) is 24.
It is absorbed by alkaline pyrogallate, but insoluble in oil of turpentine.	It is soluble in oil of turpentine.
The dissociation of oxygen molecules into atoms is highly endothermic and requires a large quantity of heat.	The decomposition of ozone into oxygen is highly exothermic.
At ordinary temperature, oxygen has no action on mercury.	Mercury in contact with ozone loses mobility and forms a thin film on the glass.
Oxygen cannot act as reducing agent.	Ozone acts as reducing agent towards certain substances.
Oxygen cannot oxidise lead sulphide under ordinary conditions.	Ozone oxidises lead sulphide to lead sulphate.
Oxygen cannot liberate iodine from KI solution.	Ozone liberates iodine from KI solution.
Oxygen has no bleaching property.	Ozone has bleaching property.

Oxygen	Ozone
Oxygen does not form addition compound with unsaturated organic compound.	Ozone forms ozonide with unsaturated compounds.
Oxygen has no action on rubber.	Ozone destroys rubber since it contains unsaturated compounds.
Oxygen acts as oxidising agent.	Ozone is a more active oxidising agent than diatomic oxygen since the decomposition of ozone into oxygen is exothermic.

EXERCISES

1. Describe the laboratory method of preparing oxygen from potassium chlorate. Describe an experiment to show that MnO_2 functions as a catalyst in the preparation of oxygen from $KClO_3$.

2. Suggest a laboratory method for preparing small amounts of oxygen from (a) lead nitrate, (b) conc. H_2SO_4 and (c) sodium peroxide.

3. Describe a method of preparing oxygen in the laboratory without the application of heat.

4. Describe the effect of heat on the following substances : (a) mercuric oxide (b) red lead (c) lead nitrate (d) potassium permanganate and (e) potassium nitrate.

5. Describe the commercial preparation of oxygen and nitrogen by the liquefaction of air.

Discuss the principles involved in the method.

6. Discuss the important physical and chemical properties of oxygen.

7. Discuss the phenomenon of combustion. Describe experiments to show combustion of the following substances :

(a) sulphur, (b) charcoal, (c) phosphorus, (d) sodium, (e) magnesium and (f) iron.

8. What is the oxygen cycle ? What are the uses of oxygen ?

9. By whom was ozone discovered ? How did it get its name ? How is ozone prepared ?

10. Describe how you would prepare pure ozone.

11. Describe some important properties of ozone. Why is ozone a more active oxidizing agent than diatomic oxygen ?

12. What is an ozoniser ? Describe Siemen's ozoniser for preparing ozonised oxygen. What are the uses of ozone ?

13. How is ozone formed in the atmosphere ? State some properties of ozone in which it acts as (a) oxidizing agent and (b) reducing agent.

14. How would you prove that ozone is an allotrope of oxygen ?

15. What do you mean by diffusion of gases ? State Graham's law of diffusion and show how this law can be applied to determine the molecular formula of ozone.

16. Explain what happens when :

- (i) ozone is passed through potassium iodide solution.
- (ii) lead nitrate is heated strongly.
- (iii) conc. sulphuric acid is added drop by drop on red-hot pumice stone.
- (iv) water is added drop by drop on sodium peroxide.
- (v) ozone is passed through hydriodic acid.
- (vi) ozonised oxygen is passed through a solution of hydrogen peroxide.
- (vii) ozone is led into a solution of stannous chloride acidified with hydrochloric acid.
- (viii) hydrogen peroxide solution is added to a solution of potassium permanganate in dilute sulphuric acid.

17. Explain the following statements :

- (a) Ozone is more active oxidising agent than oxygen.
- (b) Silent electric discharge is necessary for the formation of ozone.
- (c) Ozone has bleaching ability but oxygen is unable to bleach substances.
- (d) Ozone is unstable but oxygen is stable.

18. How would you separate oxygen from a mixture of oxygen and ozone, and oxygen from a mixture of oxygen and hydrogen.

19. Compare the properties of oxygen and ozone .

20. Prove that oxygen and ozone are primarily the same element. [H. S., '80.]

21. Prove experimentally that ozone is a more powerful oxidising agent than oxygen.

CHAPTER III

WATER AND HYDROGEN PEROXIDE

Hydrogen forms two oxides : (i) Water, H_2O and (ii) hydrogen peroxide, H_2O_2. Water is one of the most important chemical substances.

Water

The ancient chemists regarded water to be one of their four elements, namely, fire, air, water and earth. It was hence a revolutionary discovery when in 1781, H. C. Cavendish showed that water is obtained by exploding a mixture of "one volume of oxygen and two volumes of inflammable air (hydrogen)". Lavoisier repeated the Cavendish's experiments and proved conclusively that water is not an element but a compound of hydrogen and oxygen.

Water is the most abundant substance on earth. The total amount of water on earth is estimated to be 2×10^{18} tons. It occurs in nature in three states :

(i) **in solid state**—Water lies in immense quantities as snow and ice on the peaks of high mountains and in the polar regions. Water is contained in plant, and animal structures and in many minerals. It comprises about 65% of the human body. Fruits and vegetables may contain as much as 94% of water. It occurs as "water of crystallization" in many rocks and minerals such as gypsum, $CaSO_4.2H_2O$.

(ii) **in the liquid state**—Liquid water is concentrated in oceans, rivers and lakes. Oceans, rivers and lakes cover three fourths of the earth's surface. Water is present not only on the surface of the earth, but also in its depth, forming the source of springs and fountains.

(iii) **in the gaseous state**—It occurs in the atmosphere as water vapour ; as much as 50,000 tons of water vapour can be present in the air over one square mile of the earth's surface.

Natural waters. Water is abundantly distributed in nature. Natural water is never pure and always contains many impurities. Some of these impurities are in suspension, others in solution. The nature and amounts of impurities present vary with the source of water. Hence, natural waters are divided, according to the sources from which they are obtained, into the following classes.

(i) **Rain water.** The water vapour present in the atmosphere condenses on cooling as rain, hail or snow. Rain water is the purest form of natural water, but even it contains various gaseous impurities such as oxygen, carbon dioxide, nitrogen and solid impurities such as ammonium nitrate, which is formed during thunderstorms. They entrap these impurities from air when they fall. Rain water when collected near the sea in high winds contains sodium chloride and if collected near towns, contains sulphur dioxide and sulphuric acid formed by the burning of coal containing iron pyrites. They also contain insoluble matter such as particles of dust, pollen grains and bacteria.

(ii) **Spring and Mineral water.** Falling on the earth, rain water percolates through the porous strata of the soil. In its journey underground, the percolating water loses suspended impurities owing to filtration through porous strata and organic matters owing to oxidation by soil bacteria but dissolves various soluble substances such as compounds of calcium, magnesium and sodium. Sooner or later water which has percolated underground will be forced to the surface as spring water. Since the spring water is free from suspended and organic impurities, it is often suitable as drinking water.

When the spring water contains an unusual amount of some particular mineral constituent which gives it a marked taste or some specific properties such as medicinal properties, it is known as mineral water. Mineral waters are of various types. (i) *Chalybeate* waters contain ferrous bicarbonate to which medicinal properties are attributed. (ii) *Sulphur waters* or Hepatic waters contain hydrogen sulphide, alkaline sulphide and other sulphur compounds. (iii) *Saline* waters or Bitter waters contain the various salts such as sulphate and chloride of magnesium and sodium, which give the water a bitter taste. This water is used as aperient. (iv) *Iodine* waters contain iodine compounds. (v) *Acidulous* waters contain carbon dioxide in the dissolved state. (vi) *Alkaline* waters contain sodium bicarbonates and lithium bicarbonates. This water is used in the treatment of gout. (vii) The waters of some springs (hot springs) issue at an elevated temperature. These waters are known as thermal waters and contain traces of radium emanation to which a special medicinal value is attributed.

(iii) **River water.** Rain water drains partly into streams and rivers. Hence, river water contains not only the inorganic impurities such as chlorides, sulphates, carbonates and bicarbonates of sodium, potassium, calcium, magnesium and iron dissolved out from the soil and rocks, but also organic matter derived from plants growing on the sides and bottom of the river. The soluble bicarbonates of calcium and magnesium are formed by the action of dissolved carbon dioxide on insoluble carbonates of calcium and magnesium when the river flows through the rocks containing calcium and magnesium carbonate ; e.g.,

$$CaCO_3+H_2O+CO_2 = \underset{\text{(calcium bicarbonate)}}{Ca(HCO_3)_2}$$

$$MgCO_3+H_2O+CO_2 = \underset{\text{(magnesium bicarbonate)}}{Mg\,(HCO_3)_2}$$

River water also contains colloidal solids held in suspension which are precipitated by mineral salts where the river flows into the sea, giving rise some times to the formation of deltas.

(iv) **Sea water.** Rivers flow into the sea carrying their dissolved impurities and suspended matter which have not been deposited in transit. Hence, sea water contains largest amount of dissolved impurities—about 3·6% of solids in solution of which 2·6% is the common salt. The ratio of sodium to potassium in sea water is high because the soil preferentially retains potassium salts. An average type of sea water has the composition as : 96·5% of water, 2·7% of sodium salts ; 0·07% of potassium salts ; 0·14% of calcium salts ; 0·59% of magnesium salts ; 0·012% of nitrogen ; 0·006% of oxygen and 0·017% of carbon dioxide.

The vapour which rises from the sea by evaporation is almost pure water, hence sea water must be gradually becoming more and more salty ; the more the evaporation, the more is the proportion of salts in solution. Thus, the mediterranean sea with high evaporation contains 3·9% of the salts ; the Black sea and the Baltic sea with less evaporation contains 1·8% and 0·5% of the salts respectively.

Soft and Hard water. Waters which contain dissolved impurities can be classed as soft or hard depending upon the action of soap on them.

(a) **Soft water.** Water which produces lather easily with soap is called soft water. Soft waters are comparatively free from mineral salts. Rain water is a soft water which contains very little dissolved salts.

(b) **Hard water.** Water which produces lather only with difficulty is known as hard water. The hardness of water is due to presence of a large quantity of calcium, magnesium and iron salts (generally salts of any metal other than an akali metal) which react with the soap and form an insoluble precipitate. Hard water forms a large amount of scale on the walls of boilers ; it is very difficult to soften meat and vegetables by boiling them in hard water.

Soaps are the sodium and potassium salts of certain fatty acids. Typical soap contains sodium palmitate, $C_{15}H_{31}COONa$, sodium stearate, $C_{17}H_{35}COONa$, and sodium oleate, $C_{18}H_{37}COONa$. When a soap containing sodium palmitate is treated with water, sodium palmitate goes into solution and reacts with calcium, magnesium and iron salts present in hard water as follows :

$$\underset{\text{(Sodium palmitate or sodium soap)}}{2C_{15}H_{31}COONa} + Ca(HCO_3)_2 = \underset{\text{(Calcium palmitate or calcium soap)}}{(C_{15}H_{31}COO)_2Ca} + 2NaHCO_3$$

Sodium palmitate is quite soluble in water but the palmitates of calcium, magnesium and iron are very insoluble in water and are, therefore, obtained in the form of a precipitate. Hard water will, therefore, form a lather when all the calcium, magnesium and iron present in it are removed as precipitates. The scum which is noticed when soap is used with hard water is the precipitates of calcium, magnesium and iron soaps.

There are two types of hardness—(i) temporary hardness and (ii) permanent hardness.

Temporary hardness. Hardness which is due to the presence of bicarbonates of calcium, magnesium and iron in water is called temporary hardness. Temporary hardness can be removed by easy means such as boiling. The process of removing calcium, magnesium and iron salts from hard water is called the softening of water.

Softening temporary hardness of water. (a) **By boiling.** When the water containing the soluble calcium, magnesium or iron bicarbonates is boiled, carbon dioxide is evolved and the precipitates of calcium, magnesium and iron carbonates are obtained :

$$Ca(HCO_3)_2 = CaCO_3 + H_2O + CO_2$$

$$Mg(HCO_3)_2 = MgCO_3 + H_2O + CO_2$$

$$Fe(HCO_3)_2 = FeCO_3 + H_2O + CO_2$$

Since the ferrous carbonate is readily oxidised by atmospheric oxygen, a precipitate of ferric hydroxide is obtained :

$$4FeCO_3 + 6H_2O + O_2 = 4Fe(OH)_3 + 4CO_2$$

Since magnesium carbonate is appreciably soluble in water, magnesium cannot be completely removed by boiling. Again, this method is too expensive for softening temporary hard water on a large scale.

(iii) **Clark's process.** This process depends upon the fact that the slaked lime, $Ca(OH)_2$ reacts with calcium bicarbonate and magnesium bicarbonate present in water to form normal calcium carbonate and magnesium carbonate which are precipitated.

$$Ca(HCO_3)_2 + Ca(OH)_2 = 2CaCO_3 + 2H_2O$$

$$Mg(HCO_3)_2 + Ca(OH)_2 = MgCO_3 + CaCO_3 + 2H_2O$$

The appreciably soluble magnesium carbonate which is formed, then reacts with more lime to form insoluble magnesium hydroxide.

$$MgCO_3 + Ca(OH)_2 = Mg(OH)_2 + CaCO_3$$

Hence, if magnesium bicarbonate is present, double the amount of lime must be added in order to precipitate magnesium hydroxide. Calculated amount of slaked lime is to be added because if too much slaked lime is added, free Ca^{++} ions enter into the water by solution of lime and the water again becomes hard.

Water to be softened is run in a large settling tank and mixed with a calculated* quantity of clear lime water and the precipitates formed are allowed to settle down at the bottom of the tank. On separation the carbonates carry down with them the greater part of the suspended and dissolved organic matter and, therefore, a little more than the calculated quantity of lime water is always added. Since water thus treated settles with difficulty, it is convenient to filter it by means of beds of sands and gravel in order to obtain a perfectly clear water.

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* 1 litre of saturated clear solution of slaked lime contains 1·3 grams of $Ca(OH)_2$. 600 c.c. of this solution are required for each French degree of temporary hardness per 100 litres of water. 1 French degree=0·7 English degree.

(ii) **Permanent hardness.** The hardness which is caused by the presence of the chlorides and sulphates of calcium, magnesium or iron in solution in water, is called permanent hardness. They are called permanent hard water because such water cannot be softened by easy means such as boiling but can be softened only by chemical methods. These waters may, in addition, possess temporary hardness.

Softening permanent hardness of water. (*a*) **Lime-soda process.** The temporary hardness, if present, is removed by boiling or by Clark's process. Permanent hardness can be removed by the addition of sodium carbonate to water. Sodium carbonate reacts with the chlorides and sulphates of calcium, magnesium or iron to form the insoluble calcium, magnesium or ferrous carbonate :

$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4$$
$$MgCl_2 + Na_2CO_3 = MgCO_3 + 2NaCl$$
$$CaCl_2 + Na_2CO_3 = CaCO_3 + 2NaCl$$

Both temporary and permanent hardness can be removed simultaneously by adding calculated quantity of lime and soda to the water ; a little caustic soda is some times also added. If magnesium chloride is present, it reacts with lime to form insoluble magnesium hydroxide :

$$MgCl_2 + Ca(OH)_2 = Mg(OH)_2 + CaCl_2$$

The calcium chloride thus formed then reacts with sodium carbonate to form insoluble calcium carbonate :

$$CaCl_2 + Na_2CO_3 = CaCO_3 + 2NaCl$$

Sodium hydroxide reacts with calcium bicarbonates as follows :

$$Ca(HCO_3)_2 + 2NaOH = CaCO_3 + Na_2CO_3 + 2H_2O$$

The precipitates which are obtained are usually finely divided and settle only with difficulty. For this reason, a small amount of aluminium sulphate, alum or ferric sulphate is often added as a coagulant. This reacts with lime to form flocculent, gelatinous precipitates of hydroxides :

$$Fe_2(SO_4)_3 + 3Ca(OH)_2 = 2Fe(OH)_3 + 3CaSO_4$$

These precipitates then carry down the finely divided precipitates obtained after treating water with lime and soda to the bottom of the tank. These precipitates are then separated by filtering through beds of sand or a filter press.

Waters softened by soda-lime process are used in boilers and laundries.

(ii) **Cation-exchange, permutit or zeolite method.** The most important method of softening water which has found wide application in industry is by ionic exchange. The active chemical agent in these exchanges is usually a granular, synthetic sodium aluminosilicate $Na_2Al_2Si_2O_8, nH_2O$. Such aluminosilicates are known as zeolites. Zeolites may be either naturally occurring or synthetic— the synthetic zeolite which is produced by fusing quartz, alumina and sodium carbonate is known as permutit. When hard water is passed through a bed of zeolites, calcium, magnesium or iron ions present in water are exchanged by the zeolite for the sodium ions. If the formula of zeolite is taken as Na_2Z where Z stands for the zeolite radical ; then the reactions which take place can be represented by the following equations :

$$\begin{aligned}
&Ca(HCO_3)_2 + Na_2Z \rightleftharpoons CaZ + 2NaHCO_3\\
&CaSO_4 + Na_2Z \rightleftharpoons CaZ + Na_2SO_4\\
&MgSO_4 + Na_2Z \rightleftharpoons MgZ + Na_2SO_4\\
&Mg(HCO_3)_2 + Na_2Z \rightleftharpoons MgZ + 2NaHCO_3
\end{aligned}$$

Both sodium and calcium, magnesium or iron zeolites are insoluble in water and hence are retained in the bed.

When all the sodium in the zeolite is replaced by calcium, magnesium or iron, the zeolite loses its ability to soften water. But it can be easily regenerated by passing a strong sodium chloride solution through the bed. This causes the reverse reaction to take place ; the calcium ions being replaced by sodium ions and the original sodium zeolites are formed :

$$\begin{aligned}
&CaZ + 2NaCl \rightleftharpoons CaCl_2 + Na_2Z\\
&MgZ + 2NaCl \rightleftharpoons MgCl_2 + Na_2Z
\end{aligned}$$

The Ca^{++}, Mg^{++} and Fe^{++} ions are removed as the soluble chlorides and, therefore, the same bed of sodium zeolite can be used over and over again. In this method, only sodium chloride is consumed ; and both the temporary and permanent hardness can be removed simultaneously.

Procedure. The apparatus consists of a tank which contains a bed of zeolite between two beds of gravel (fig. 3.1). Hard water enters from the inlet at the top and percolates through the beds of gravel and zeolite. The softened water comes out through the outlet at the bottom. When a specified quantity of hard water has been softened, the inlet is closed and a strong solution of sodium chloride is allowed to percolate through the beds from a reservoir at the top of the tank ; the bed is thus regenerated and again used for softening hard water.

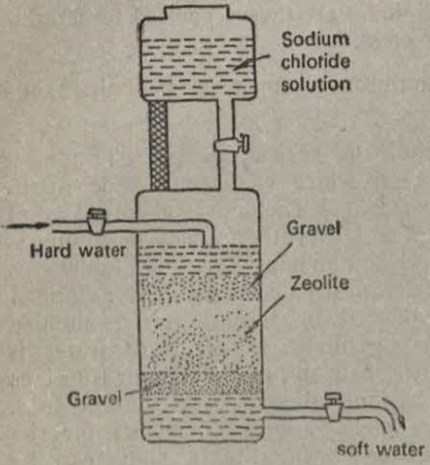

Fig. 3.1 : Softening of hard water by zeolite process.

(ii) **Calgon process.** This method of softening water which is used on a small scale depends upon the fact that when sodium hexametaphosphate which is commercially known as calgon is added to hard water, it ties up calcium, magnesium or iron present in hard water and prevents their precipitation while the water is being used. Calcium, magnesium or iron salts combine with sodium hexametaphosphate, displacing sodium and forming a stable complex salt :

$$Na_2[Na_4(PO_3)_6]+CaSO_4=Na_2[Na_2Ca(PO_3)_6]+Na_2SO_4$$

The complex salt is so stable that calcium cannot be precipitated as boiler scale or as insoluble calcium soap when water is boiled or treated with soap. On the other hand, if a scale is already formed in a boiler, then it is gradually redissolved. Calgon is used in laundries for softening water.

Estimation of hardness. The hardness of water is expressed in degrees. Each degree of hardness represents the hardness produced by one part of calcium carbonate (or its equivalent) in 100,000 parts of water[*] (1 milligram per litre of water is identical with 1 part in million (1000,000) parts of water). A degree of hardness is some times defined as 1 grain of calcium carbonate or its equivalent per gallon of water. 1 grain per gallon is equal to 17·1 parts per million (ppm).

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[*] 1 part of $CaCO_3$ or its equivalent is present in 1000000 parts of water.

∴ 1 gram of $CaCO_3$ or its equivalent is present in 1000,000 c.c. of water. [∵ density of water=1]

∴ 1 mg of $CaCO_3$ or its equivalent is present in 1000 c.c. or 1 litre of water.

∴ 1 ppm≡1 mg of $CaCO_3$ or its equivalent per litre of water.

Hence, water whose hardness is 1 ppm (1 part in 1000,000 parts of water) contains 1 milligram of $CaCO_3$ or its equivalent per litre. Since 1° hardness of water is produced by one part of $CaCO_3$ or its equivalent in 100,000 parts of water, 1° is equal to 10 ppm. Hence, water whose hardness is 1° or 10 ppm contains 10 milligram of $CaCO_3$ or its equivalent per litre.

A water less than 10° hardness (or 100 ppm) may be called soft ; a water between 18° and 20° hardness is "moderately hard" ; a water between 20° to 30° hardness is "hard" and a water over 30° hardness is "very hard". Domestic water with hardness less than 100 ppm (or 10°) is good and that with hardness between 100 ppm and 200 ppm (or 20°) is fair.

In order to estimate the degree of hardness of water, the hard water is titrated with a standard soap solution until the lather produced by shaking the mixture vigorously, lasts for five minutes. A soap solution (obtained by dissolving soap in methylated spirit) is standardised by titration against water which contains a known concentration of calcium chloride.

Purification of water. (a) **For laboratory use.** Water for laboratory use must be entirely devoid of impurities. Such very pure water can be obtained from natural water by distillation and by anion and cation exchange.

By anion and cation exchange. A technique for getting very pure or de-ionised water is ion-exchange. The most commonly used material in this process are the ion-exchange resins. There are two types of ion-exchange resins : (i) cation-exchange resins which may be formulated as $ReSO_3H$. These resins are capable of exchanging their hydrogen ions for metal ions. (ii) anion-exchange resins which may be formulated as $ReNH_2$. These resins are capable of binding the negative ions or anions.

The water is first freed from bacterial matter by treatment with chlorine. This water is passed through tank A containing cation-exchange resin column, when cation impurities present in water are exchanged for hydrogen ions in the resins. This exchange reaction can be represented by the following equations :

$$2ReSO_3H + Ca(HCO_3)_2 \rightleftharpoons (ReSO_3)_2Ca + 2H_2CO_3$$
$$2ReSO_3H + CaSO_4 \rightleftharpoons (ReSO_3)_2Ca + H_2SO_4$$
$$ReSO_3H + NaCl \rightleftharpoons ReSO_3Na + HCl$$

As a result of these reactions, cations are trapped on the resins and any solution containing salts such as $Ca(HCO_3)_2$, $CaSO_4$, NaCl, etc., is converted into a solution of the corresponding acids (H_2CO_3, H_2SO_4, HCl, etc.).

To remove these acids water is now passed through tank B containing anion-exchange resins ; the acids are then bound as a

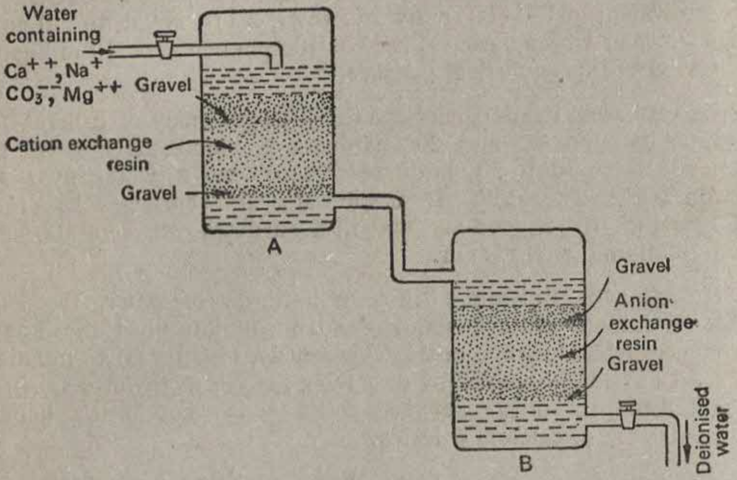


Fig. 3.2

result of the formation of insoluble salts. The reactions which take place can be represented by the following equations :

$$ReNH_2 + HCl = [ReNH_3]Cl$$
$$2ReNH_2 + H_2SO_4 = [ReNH_3]_2SO_4$$

The water which passes out of the tank B contains practically no ions and is known as deionised water. It may be used in the laboratory and in industrial processes in place of distilled water.

The cation-exchange resin which is left in tank A after use can be regenerated by passing moderately strong sulphuric acid through the bed :

$$(ReSO_3)_2Ca + H_2SO_4 = 2ReSO_3H + CaSO_4$$
$$2ReSO_3Na + H_2SO_4 = 2ReSO_3H + Na_2SO_4$$

The used up anion-exchange resin in tank B can be regenerated by use of a moderately concentrated solution of sodium hydroxide :

$$[ReNH_3]Cl + NaOH = ReNH_2 + NaCl + H_2O$$
$$[ReNH_3]_2SO_4 + 2NaOH = 2ReNH_2 + Na_2SO_4 + 2H_2O$$

(b) **For drinking purposes.** Potable water, that is water which is fit for human consumption, is obtained principally from rivers, lakes and wells. These waters contain dissolved air, carbon dioxide and other gases, mineral matters, suspended colloidal particles of soil, suspended solid particles of sand and clay, organic matter and bacteria. The mineral matters present in water are not injurious to health but are beneficial ; hence water for drinking purposes need not be softend. Drinking water must be free from harmful bacteria, organic matters and suspended impurities. Natural water containing nitrates in solution should be regarded as unsuitable as the nitrates originate from decaying animal matters or sewage. Again, drinking water should not be very soft because very soft water in presence of oxygen and carbon dioxide reacts with lead (from lead pipe) forming slightly soluble lead hydroxide, $Pb(OH)_2$, which is a cumulative poison.

Water from rivers is first piped into large settling basins where suspended coarse particles are allowed to settle, but finely divided particles show little inclination to settle. Water is now allowed to enter into a mixing tank where it is mixed with lime and aluminium sulphate or ferrous sulphate or other chemicals. This causes the formation of a heavy gelatinous precipitate of aluminium hydroxide that carries these finely divided suspended particles down with it as it settles in the next settling tank (B).

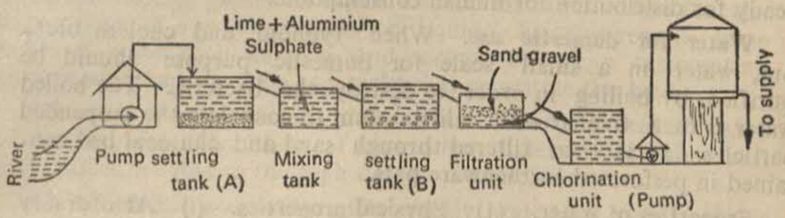


Fig. 3.3 : Purification of water for town supply.

$$3Ca(OH)_2 + Al_2(SO_4)_3 = 3CaSO_4 + 2Al(OH)_3$$

The clarified water is then filtered through beds of sand, gravel and some times charcoal. The filtered water still contains some bacteria and is passed into a tank where it is subjected to the process of disinfection. Water is disinfected by any of the following processes.

(i) **by chlorination.** Bacterial matter is removed by injecting controlled amounts of chlorine into the water. Chlorine reacts with water according to the equation

$$2Cl_2 + 2H_2O = 4HCl + O_2$$

Oxygen which is evolved oxidises (and kills) any micro-organisms present in water. Some times bleaching powder is added instead of chlorine.

In the chloramine process, a mixture of chlorine and ammonia which is more effective than chlorine alone, is added to water ; this improves greatly the taste of water.

(ii) **by ozonised air.** Water can be disinfected by bubbling ozonised air through the filtered water. An ozone molecule decomposes readily into a molecule of oxygen and an atom of oxygen which oxidises (and kills) the bacteria. After ozone treatment, water is exposed to air to render it palatable.

(iii) **by ultra violet rays.** Water is subjected to the exposure to ultra violet lights obtained from mercury vapour lamp enclosed in a quartz container, when the bacterial matters present in water are killed. This process does not affect in any way the palatibility of water.

Of all these processes, chlorination is the process which is most commonly used.

Disinfected water is now pumped up to the reservoir and is ready for distribution for human consumption.

Water for domestic use. When typhoid and cholera break out, water on a small scale for domestic purpose should be purified by boiling in order to destroy the bacteria. The boiled water is then treated with a little alum to coagulate the suspended particles. It is then filtered through sand and charcoal bed contained in perforated earthenware pots.

Properties of water. (1) **Physical properties.** (i) At ordinary temperature, pure water is a transparent liquid with no taste and odour. In thin layers, it is colourless but in thick layers it has a bluish-green colour. Water has the simplest formula H_2O ; but in the liquid state water is associated, and is represented by the general formula, $(H_2O)_n$, where n=2, 3, 4, 5, etc. Association is a phenomenon by which the simple molecules combine into more complex ones without changing the chemical nature of the substance. This can be expressed by the following equation.

$$nH_2O \rightleftharpoons (H_2O)_n$$

(ii) The density of water increases on cooling ; it has the highest density at +4°C. Above and below this temperature, water expands and its density decreases.

Many physical constants and units are defined with the help of physical properties of water. At standard pressure (1 atm), the freezing point of water is taken as 0°C and the boiling point of water at 1 atm is taken as 100°C. In the metric system, the unit of volume is chosen in such a way that 1 ml. of water weighs 1 gram at +4°C. Ice at 0°C has a density of 0·917 gram/ml. Hence, ice is lighter than water and floats on liquid water. This fact is of great importance to natural life since in cold region ice formed in water reservoirs remains on the surface of the water and protects the deeper layers of water from further cooling. If this were not the case, the whole body of water would be converted into a solid mass of ice, which the warmth of the summer would not be sufficient to melt. The expansion of water on freezing is an unusual phenomenon, since almost all other substances contract upon changing from the liquid state to the solid state and the density of the solid is greater than that of the liquid.

(iii) Pure water is a very poor conductor of electricity. This is due to the fact that it ionises very slightly into hydrogen ion and the hydroxyl ion.

$$H_2O \rightleftharpoons H^+ + OH^-$$

Addition of small quantity of an electrolyte increases the electrical conductivity of water.

Water has a higher specific heat than any other substance (solid or liquid), i.e., a greater amount of heat is required to raise the temperature of water an equal number of degrees than for the same weight of any other solid or liquid. For this reason, large bodies of water such as lakes and oceans, change in temperature more slowly than the soils and rocks that constitute the land.

The heat of vaporisation of liquid water and the heat of fusion of ice are higher than those of most other liquids. Such abnormal high values are due to the high degree of association.

(2) **Chemical properties.** Chemically, water is a very reactive substance. The manifestations of the chemical properties of water are discussed below.

(i) **Thermal stability.** The molecules of water have high stability to heat, since water is an exothermic compound. However, at 1000°C and 1 atm. pressure water vapour begins to dissociate perceptibly into hydrogen and oxygen, and at 2000°C it is only dissociated to about 1·8 per cent

$$2H_2O \rightleftharpoons 2H_2 + O_2 - 137 \text{ kcal}$$

Since this reaction goes on with the absorption of heat, the dissociation increases as the temperature is increased. Due to this slight dissociation at elevated temperature, water is able to react with various relatively inactive substances to form their oxides and to evolve hydrogen.

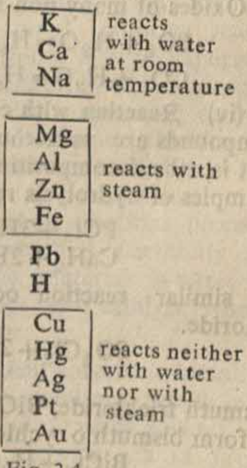

K
Ca
Na
reacts with water at room temperature
Mg
Al
Zn
Fe
reacts with steam
Pb
H
Cu
Hg
Ag
Pt
Au
reacts neither with water nor with steam

Fig. 3.4

(ii) **Reaction with metals.** Many metals which are higher in the electrochemical series than hydrogen, react with water at a suitable temperature

$$2Na + 2H_2O = 2NaOH + H_2$$
$$Ba + 2H_2O = Ba(OH)_2 + H_2$$

Water reacts with oxides of metals to form metallic hydroxides.

$$Na_2O+H_2O=2NaOH$$
$$CaO+H_2O=Ca(OH)_2$$

(iii) **Reaction with non-metals.** Water reacts with many non-metals. For example, carbon at white heat reacts with steam forming water gas.

$$C+H_2O=CO+H_2$$

Similarly, silicon reacts with water forming silicon dioxide and hydrogen.

$$Si+2H_2O=SiO_2+2H_2$$

When chlorine is passed into water, a green solution is obtained, which on standing reacts forming hydrochloric and hypochlorous acids.

$$Cl_2+H_2O=HCl+HOCl$$

In direct sunlight hypochlorous acid, HOCl, breaks up with the formation of oxygen.

$$2HOCl=2HCl+O_2$$

Fluorine reacts with water forming hydrofluoric acid and oxygen ; hypofluorous acid is obtained in no stage.

$$2F_2+2H_2O=4HF+O_2$$

Oxides of many non-metals react with water to form the acids.

$$SO_2+H_2O=H_2SO_3 \;; \qquad SO_3+H_2O=H_2SO_4$$
$$CO_2+H_2O=H_2CO_3 \;; \qquad P_2O_5+3H_2O=2H_3PO_4$$

(iv) **Reaction with compounds.** Reactions involving water and compounds are numerous. Among these is the hydrolysis reaction, that is, the decomposition of a compound by water. Some of the examples of hydrolysis reactions are given below.

$$PCl_3+3H_2O=H_3PO_3+3HCl$$
$$CaH_2+2H_2O=Ca(OH)_2+2H_2$$

A similar reaction occurs with substances such as sulphuryl chloride.

$$SO_2Cl_2+2H_2O=\underset{\text{(sulphuric acid)}}{SO_2(OH)_2}+2HCl$$

Bismuth trichloride, $BiCl_3$, undergoes hydrolysis in aqueous solution to form bismuth oxychloride.

$$BiCl_3+H_2O=BiOCl+2HCl$$

Metallic hydrides react with water to form hydrogen and the hydroxides of the metals.

$$NaH+H_2O=NaOH+H_2 \;; \quad CaH_2+2H_2O=Ca(OH)_2+2H_2$$

Cacium carbide reacts with water to form calcium hydroxide and acetylene.

$$CaC_2+2H_2O=Ca(OH)_2+C_2H_2$$

Magnesium nitride reacts with water to form magnesium hydroxide and ammonia.

$$Mg_3N_2+6H_2O=3Mg(OH)_2+2NH_3$$

Calcium cyanamide reacts with water to form calcium carbonate and ammonia.

$$CaCN_2+3H_2O=CaCO_3+2NH_3$$

(v) **Formation of addition compounds with water.** Water combines with a number of substances to form addition compounds known as hydrates. In these reactions, the properties of neither water nor the other reacting compounds are materially affected.

$$\underset{\text{(white)}}{CuSO_4}+5H_2O \rightleftharpoons \underset{\text{(blue)}}{CuSO_4,\ 5H_2O}$$

$$\underset{\text{(blue)}}{CoCl_2}+6H_2O \rightleftharpoons \underset{\text{(red)}}{CoCl_2,\ 6H_2O}$$

$$Na_2CO_3+10H_2O \rightleftharpoons Na_2CO_3,\ 10H_2O$$

That a reaction has occurred is clearly proved (i) by change in colour ; (ii) by the change in crystalline structure which accompanies many of the reactions and (iii) by the definite composition of the compounds formed.

(vi) **Water as a catalyst.** Many reactions do not take place in absence of water but proceed readily, even violently if a trace of water is present. Thus, sodium can be melted in dry chlorine without any reaction taking place, but moist chlorine reacts vigorously with sodium in the cold. Dry sulphur may be vaporised in dry oxygen without any reaction ; perfectly dry hydrogen chloride does not react with absolutely dry ammonia ; carbon monoxide does not burn in dry oxygen ; hydrogen and chlorine do not explode when perfectly dry and silver can be melted in a dry mixture of hydrogen and oxygen without an explosion taking place. In presence of a trace of moisture, these reactions proceed violently. The decay of organic matter which is essentially an oxidation process takes place only when the material is wet. In all these reactions, water is considered to act as a catalyst whose presence is necessary for the reactions to occur.

Water as a solvent. Water is an excellent solvent. Metallic salts readily dissolve in water to give solutions which are good electrolytic conductors. Water is a good ionising solvent for acids and bases. The solvent properties of water is of great importance in the complex processes of vegetable and animal life. Thus, fertility of soil is increased by water and water is the medium by which much of the food is transported to plants and to the various points of use within the bodies of the animals. Water is also the medium by which most of the waste matters are eliminated from the body.

Tests of water. (i) A minute quantity of water can be detected by the blue colour it forms with white anhydrous copper sulphate.

(ii) When a lump of freshly burnt quick lime is added to water, it crumbles to powders with hissing sound and evolving much heat.

$$CaO + H_2O = Ca(OH)_2$$

Hydrogen Peroxide

Hydrogen peroxide was discovered by L. J. Thenard in 1818. The discovery was made while investigating the action of dilute acids on barium peroxides. He called it the oxygenated water, since he showed that its formula corresponded to H_2O_2.

Hydrogen peroxide occurs only in traces in the free state. It is formed in the atmosphere in small quantities by powerful electrical discharge or by heavy snowfalls. It occurs in traces in plants. It is also produced on burning hydrogen in air, when hydrogen flame impinges on ice, and during the slow combustion of ether.

Preparation. Oxygen does not directly add to water, H_2O, to form hydrogen peroxide, H_2O_2, but it adds directly to many active metal oxides to form peroxides.

$$\underset{\text{(barium oxide)}}{2BaO} + O_2 = \underset{\text{(barium peroxide)}}{2BaO_2}$$

$$\underset{\text{(sodium oxide)}}{2Na_2O} + O_2 = \underset{\text{(sodium peroxide)}}{2Na_2O_2}$$

Hydrogen peroxide can be prepared by treating these peroxides with acids. The temperature should be kept low to prevent the decomposition of hydrogen peroxide.

(a) **From barium peroxide.** (i) **Laboratory preparation.** Hydrogen peroxide is prepared in the laboratory by the action of dilute sulphuric acid on barium peroxide.

$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2$$

Barium sulphate being insoluble in water, can be removed by filtration. Anhydrous barium peroxide does not react readily with sulphuric acid, because an insoluble coating of barium sulphate is formed on the surface of each particle. Consequently, hydrated barium peroxide (BaO_2, $8H_2O$) is used.

A thin paste of hydrated barium peroxide is made by treating finely powdered barium peroxide with water and it is gradually added to an ice-cold solution of dilute sulphuric acid (1 volume of acid to 5 volumes of water) in a beaker. The mixture is stirred vigorously by means of a glass rod. When the mixture is just acidic, the precipitate of barium sulphate formed is allowed to settle at the bottom of the beaker, and then filtered off. The filtrate which contains excess H_2SO_4 is neutralised by adding a little barium hydroxide and is filtered again. The filtrate is an aqueous solution of 10 to 20% hydrogen peroxide. The solution is usually stabilised by adding some preservative such as glycerol. The precipitate of barium sulphate is a valuable by-product used as a pigment known as blanc fixe.

N. B. (i) In the preparation of hydrogen peroxide, conc. H_2SO_4 is not used because much heat is evolved by the action of conc. H_2SO_4 on barium peroxide. This heat decomposes the hydrogen peroxide formed. For this reason, ice-cold solution of dilute sulphuric acid is used in the preparation of hydrogen peroxide.

(ii) Anhydrous barium peroxide is not used in the preparation of hydrogen peroxide because heat evolved by the reaction of anhydrous barium peroxide and the acid decomposes the hydrogen peroxide formed into water and oxygen. Again, within a very short time after the reaction has started, an isoluble coating of barium sulphate is formed on each particle of anhydrous barium peroxide. This coating prevents barium peroxide from coming in contact with sulpuric acid. As a result, the reaction ceases.

(iii) After the reaction is complete, the solution must be acidic because in presence of excess barium peroxide hydrogen peroxide formed begins to decompose. Again, the acid increases the stability of hydrogen peroxide solution, i.e., it acts as a negative catalyst in the decomposition of hydrogen peroxide.

(iv) Dil. HCl is not used in the preparation of hydrogen peroxide because barium chloride formed by the action of hydrochloric acid on barium peroxide is soluble in water and is difficult to remove from the solution of hydrogen peroxide.

(v) A thin paste of hydrated barium peroxide is first made by treating finely ground barium peroxide with water because anhydrous barium peroxide does not readily react with dil. H_2SO_4 owing to the formation of insoluble coating of barium sulphate on the particles of anhydrous barium peroxide.

(ii) Phosphoric acid also reacts with barium peroxide to form hydrogen peroxide and barium phosphate.

$$3BaO_2 + 2H_3PO_4 = Ba_3(PO_4)_2 + 3H_2O_2$$

The barium phosphate formed being insoluble in water, can be separated by filtration. The use of phosphoric acid is preferred in the sense that a trace of it helps to stabilise the hydrogen peroxide formed.

A paste of barium peroxide is added slowly to a cold solution of phosphoric acid in a beaker. The mixture is stirred well and the precipitated barium phosphate is filtered off. The clear filtrate is an aqueous solution of hydrogen peroxide.

(iii) Even carbonic acid (carbon dioxide dissolved in water) is sufficiently strong to form hydrogen peroxide from barium peroxide.

$$\begin{aligned} CO_2 + H_2O &= H_2CO_3 \\ BaO_2 + H_2CO_3 &= BaCO_3 + H_2O_2 \\ \hline BaO_2 + CO_2 + H_2O &= BaCO_3 + H_2O_2 \end{aligned}$$

The barium carbonate formed is insoluble in water and hence can be separated by filtration. This method works well with anhydrous barium peroxide.

A stream of pure carbon dioxide is passed through an ice-cold suspension of finely powdered barium peroxide in water, when a precipitate of insoluble barium carbonate and an aqueous solution of hydrogen peroxide are obtained. The precipitate is filtered off, leaving an aqueous solution of hydrogen peroxide.

(b) **From sodium peroxide** (i) **Merck's process.** A 30% solution of hydrogen peroxide is prepared by adding slowly a calculated quantity of sodium peroxide to 20% ice-cold sulphuric acid solution.

$$Na_2O_2 + H_2SO_4 = Na_2SO_4 + H_2O_2$$

Most of the sodium sulphate formed is removed from the solution as decahydrate, $Na_2SO_4, 10H_2O$, by crystallisation. The solution is then distilled in vacuo. The distillate which is a 30% solution of hydrogen peroxide, is known as **Merck's perhydrol.**

(ii) A strong solution of hydrogen peroxide can be prepared in the laboratory by the action of sodium dihydrogen phosphate on sodium peroxide.

$$Na_2O_2 + 2NaH_2PO_4 = 2Na_2HPO_4 + H_2O_2$$

A calculated quantity of sodium peroxide is added to a saturated solution of sodium dihydrogen phosphate cooled in ice. Most of the disodium hydrogen phosphate formed separates as crystals of $Na_2HPO_4, 12H_2O$, and is removed by filtration. The filtrate is then cooled in a mixture of salt and ice when the remaining disodium hydrogen phosphate and some ice separate out as crystals. These crystals are then filtered off—the filtrate is a strong solution of hydrogen peroxide.

Preparation of anhydrous hydrogen peroxide. Hydrogen peroxide is less volatile than water (b. pt. of water, 100°C ; of hydrogen peroxide, 151°C). So when an aqueous solution of hydrogen peroxide in an open dish is evaporated on a water-bath at 70°C, the more volatile water vaporises away. The process is continued until the signs of effervescence appear. At this stage, the solution contains 60% hydrogen peroxide. The concentrated aqueous solution of hydrogen peroxide thus obtained on successive distillations under reduced pressure, yields a solution containing 99·1% hydrogen peroxide.

When a 95% solution of hydrogen peroxide is cooled to −10°C and seeded with a small crystal of solid hydrogen peroxide (small crystals of hydrogen peroxide are obtained by cooling 95% solution in solid carbon dioxide mixed with ether), small needle shaped crystals of pure hydrogen peroxide separate.

Industrial preparation. Pietsch-Adolf process. Commercially, hydrogen peroxide is largely manufactured electrolytically. When moderately concetrated sulphuric acid is electrolysed, hydrogen is produced at the cathode and peroxydisulphuric acid at the anode.

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$$

At anode : $2HSO_4^- = H_2S_2O_8 + 2e$

At cathode : $2H^+ + 2e = H_2$

Peroxydisulphuric acid reacts with water to form first permonosulphuric acid (H_2SO_5) and then hydrogen peroxide.

$$H_2S_2O_8 + H_2O = H_2SO_5 + H_2SO_4$$

$$H_2SO_5 + H_2O = H_2O_2 + H_2SO_4$$

Hydrogen peroxide formed is then separated by distillation.

A 50 per cent solution of sulphuric acid is electrolysed with platinum electrodes under a high current density, whereby peroxydisulphuric acid is produced. This is distilled under low pressure in a special apparatus so designed that the vapour is rapidly separated. On distillation, peroxydisulphuric acid reacts with water producing hydrogen peroxide, a 30% solution of which is obtained in the distillate. Suphuric acid is returned to the electrolytic cell for the preparation of more of the peroxydisulphuric acid. Thus, the method consumes only water and electricity.

Ammonium bisulphate can also be used instead of sulphuric acid. The electrolysis of a solution of ammonium bisulphate produces hydrogen at the cathode and ammonium peroxydisulphate at the anode.

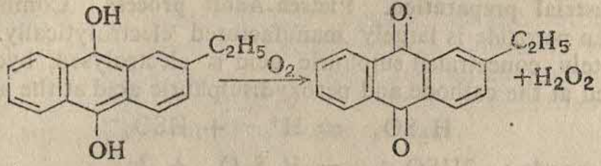
$$2(NH_4)HSO_4 = (NH_4)_2S_2O_8 + H_2$$

Ammonium peroxydisulphate then undergoes hydrolysis to produce hydrogen peroxide.

$$(NH_4)_2S_2O_8 + 2H_2O = 2(NH_4)HSO_4 + H_2O_2$$

Hydrogen peroxide is then separated by distillation. It is possible to boil away most of the water from aqueous solution of hydrogen peroxide in a fractionating column and obtain a solution of 90% hydrogen peroxide. The Pietsch-Adolf process has been developed in Germany for the manufacture of high-test hydrogen peroxide of about 90 per cent concentration.

By auto-oxidation of anthraquinol. When air is passed through a solution of 2-ethyl anthraquinol in benzene or in other suitable solvent, 2-ethyl anthraquinol is oxidised to 2-ethyl anthraquinone and hydrogen peroxide is formed.



(2-ethyl anthraquinol) (2 ethyl anthraquinone)

Hydrogen peroxide is extracted with water from the organic solvent when aqueous solution of hydrogen peroxide is formed.

After the separation of hydrogen peroxide, hydrogen is passed through the solution of anthraquinone in presence of palladium catalyst when anthraquinone is reduced again to anthraquinol. Anthraquinol can be again used for the production of hydrogen peroxide. Hence, in this process only hydrogen and oxygen are used.

Properties of hydrogen peroxide. (A) Physical properties. Anhydrous hydrogen peroxide is a syrupy liquid. In small quantities, it appears to be colourless but in large quantities it has a delicate blue colour. It has a bitter metallic taste and has an acrid, irritating odour. When a drop of hydrogen peroxide comes in contact with skin, it forms a white blister. It solidifies at −1·7°C into needle like crystals. Under normal pressure (760 mm of Hg) it boils at 151°C. It can be distilled safely under reduced pressure (b. pt. at 26 mm is 69·2°C).

(B) Chemical properties. (i) Thermal decomposition. Hydrogen peroxide is very unstable to heat and readily decomposes into water and oxygen. During decomposition, a considerable amount of heat is set free.

$$2H_2O_2 = 2H_2O + O_2 + 46{,}900 \text{ calories}$$

Its decomposition is accelerated by many substances such as finely divided or colloidal metals (e.g., platinum and manganese), bases, many salts and manganese dioxide. It may explode violently in presence of these substances. It may be decomposed by rough surfaces and by ultraviolet light. At the same time, there are few substances which can retard the decomposition of hydrogen peroxide. Such substances are, for example, small quantities of acid, calcium chloride, alcohol, glycerine, etc., that is, these substances act as negative catalysts.

When hydrogen peroxide decomposes, part of the oxygen is oxidised and part is reduced.

$$2H_2\overset{(-1)}{O_2} = 2H_2\overset{(-2)}{O} + \overset{(0)}{O_2}$$

Thus, half of the oxygen atoms is reduced to $\overset{(-2)}{O}$ which forms water and the other half is oxidised to $\overset{(0)}{O}$, i.e., free oxygen. Therefore, this reaction is an auto-oxidation and reduction process.

(ii) **Oxidising properties.** Hydrogen peroxide acts as a powerful oxidising agents. As an oxidising agent, $[O_2]^{-2}$ ion receives two electrons turning into negative oxygen ions.

$$[O_2]^{-2}+2e=2O^{-2}.$$

The following examples will clarify the above phenomenon.

(a) It liberates iodine from acidified potassium iodide solution.

$$\overbrace{H_2[O_2]^{-2}+2\overset{+1}{K}\overset{-1}{I}}^{2e} + 2HCl = 2KCl + I_2 + 2H_2\overset{-2}{O}$$

The $[O_2]^{-2}$ ion receives 2 electrons donated by two I^- ions. Hence, $[O_2]^{-2}$ ion is reduced to O^{-2} ion and I^- ion is oxidised to iodine. This reaction is quantitative and may be used for the estimation of hydrogen peroxide.

(b) It oxidises black lead sulphide into white lead sulphate.

$$PbS + 4H_2O_2 = PbSO_4 + 4H_2O$$

Use of this reaction is made in restoring discoloured oil paintings. The "white lead" paints (containing the basic carbonate, $2PbCO_3$, $Pb(OH)_2$ which have been blackened due to the formation of black lead sulphide (PbS is formed by the reaction of H_2S present in the atmosphere with basic lead carbonate) can be bleached by washing with hydrogen peroxide when black lead sulphide is converted into white lead sulphate.

(c) Ferrous salts in acid solution are oxidised to ferric salts.

$$2FeSO_4+H_2SO_4+H_2O_2=Fe_2(SO_4)_3+2H_2O$$

(d) Hydrogen peroxide oxidises arsenious acid to arsenic acid ; sulphurous acid to sulphuric acid and nitrous acid to nitric acid.

$$\underset{\text{(arsenious acid)}}{H_3AsO_3} + H_2O_2 = \underset{\text{(arsenic acid)}}{H_3AsO_4} + H_2O$$

$$\underset{\text{(sulphurous acid)}}{H_2SO_3} + H_2O_2 = \underset{\text{(sulphuric acid)}}{H_2SO_4} + H_2O$$

$$\underset{\text{(nitrous acid)}}{HNO_2} + H_2O_2 = \underset{\text{(nitric acid)}}{HNO_3} + H_2O$$

(e) Hydrogen peroxide liberates sulphur from sulphuretted hydrogen and iodine from hydriodic acid.

$$H_2S+H_2O_2=S+2H_2O$$

$$2HI+H_2O_2=I_2+2H_2O$$

(f) Hydrogen peroxide oxidises a solution of potassium dichromate acidified with sulphuric acid to a blue perchromic acid.

Perchromic acid is very. unstable and decomposes into oxygen and chromic sulphate. Perchromic acid is more stable in ether than in water.

$$3H_2O_2 + H_2Cr_2O_7 = \underset{\text{(perchromic acid)}}{2HCrO_5} + 3H_2O$$

$$2HCrO_5 + 3H_2SO_4 = Cr_2(SO_4)_3 + 4H_2O + 3O_2$$

The oxidation number of each oxygen atom in H_2O_2 is -1 while the usual oxidation number of oxygen is -2. It is the existence of oxygen in the unusual oxidation state of -1 and the tendency of the oxygen to attain its more common oxidation number of -2, which confer strong oxidising properties on hydrogen peroxide.

(iii) **Reducing properties.** During reactions with strong oxidising agents, hydrogen peroxide may manifest reducing properties. When it so acts, elemental oxygen is one of the products ; thus :

(a) Hydrogen peroxide reduces chlorine to hydrogen chloride.

$$\overset{2e}{\overleftarrow{\overset{(0)}{Cl_2} + \overset{(-2)}{H_2O_2}}} = 2\overset{(+1)(-1)}{HCl} + \overset{(0)}{O_2}$$

The reducing agent, in this case, is $\overset{-2}{O_2}$ ion which donates two electrons to chlorine atoms (i.e., reduces the chlorine atoms) and is itself oxidised to neutral O_2 molecules.

(b) Hydrogen peroxide reduces oxides of silver, platinum and other heavy metals to the corresponding metals :

$$Ag_2O + H_2O_2 = 2Ag + H_2O + O_2$$

It reduces lead dioxide to lead monoxide.

$$PbO_2 + H_2O_2 = PbO + H_2O + O_2$$

(c) An acidified solution of potassium permanganate is readily reduced and decolourised by hydrogen peroxide with the evolution of oxygen.

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$$

(d) The oxidising and reducing action of hydrogen peroxide is not only dependent on the specific nature of the substance with which it is placed in contact but also dependent upon the nature of the medium. Thus, manganese dioxide liberates oxygen from hydrogen peroxide in netural solution ; its effect is apparently catalytic.

In acid solution, hydrogen peroxide reduces manganese dioxide to manganous salts.

$$MnO_2 + H_2O_2 + H_2SO_4 = MnSO_4 + 2H_2O + O_2$$

In alkaline solution, hydrogen peroxide will effect the reverse reaction, converting manganous salts to manganese dioxide.

$$MnSO_4+H_2O_2+2NaOH=MnO_2+2H_2O+Na_2SO_4$$

Similarly, an acid solution of potassium ferrocyanide is oxidised by hydrogen peroxide to potassium ferricyanide.

$$2K_4[Fe(CN)_6]+2HCl+H_2O_2=2K_3[Fe(CN)_6]+2KCl+2H_2O$$

An alkaline solution of potassium ferricyanide is reduced to potassium ferrocyanide by hydrogen peroxide with the evolution of oxygen.

$$2K_3[Fe(CN)_6]+2KOH+H_2O_2=2K_4[Fe(CN)_6]+2H_2O+O_2$$

(e) Ozone is slowly reduced by hydrogen peroxide to oxygen.

$$O_3+H_2O_2=2O_2+H_2O$$

Solutions of bleaching powder and sodium hypobromite are reduced by hydrogen peroxide with the evolution of oxygen.

$$NaOBr+H_2O_2=NaBr+H_2O+O_2$$

(iv) **Acid properties.** Hydrogen peroxide may act as a dibasic acid. Thus, pure hydrogen peroxide turns blue litmus red. When a solution of sodium carbonate is added drop by drop to a concentrated solution of hydrogen peroxide, sodium peroxide is formed and carbon dioxide is evolved.

$$Na_2CO_3+H_2O_2=Na_2O_2+H_2O+CO_2$$

When an excess of carbonate is present, it catalytically decomposes hydrogen peroxide to evolve oxygen.

Hydrogen peroxide reacts with barium hydroxide to form barium peroxide.

$$Ba(OH)_2+H_2O_2=BaO_2+2H_2O$$

Hence, all the peroxides such as Na_2O_2, BaO_2, etc., may be regarded as salts of the diprotic acid HOOH.

$$H_2O_2+H_2O \rightleftharpoons H_3O^++HO_2^-$$
$$HO_2^-+H_2O \rightleftharpoons H_3O^++O_2^{--}$$

(v) **Formation of peroxy-acids.** Hydrogen peroxide unites with acid anhydrides to form the corresponding peroxy-acids in a manner similar to that in which water unites :

$$H_2O_2+SO_3 = \underset{\text{(peroxy sulphuric acid)}}{H_2SO_5} \quad ; (H_2O+SO_3=H_2SO_4)$$

$$H_2O_2+2SO_3 = \underset{\text{(peroxy disulphuric acid)}}{H_2S_2O_8} \quad ; (H_2O+2SO_3=H_2S_2O_7)$$

$$2H_2O_2+H_2O+P_2O_5 = \underset{\text{(peroxy phosphoric acid)}}{2H_3PO_5} \; ; (3H_2O+P_2O_5=2H_3PO_4)$$

(vi) **Formation of addition compounds.** Some salts form addition compounds with hydrogen peroxide. Thus, with ammonium sulphate it forms the compound $(NH_4)_2SO_4, H_2O_2$ and with urea it forms $CO(NH_2)_2, H_2O_2$. In these compounds, hydrogen peroxide behaves as water of crystallisation. The crystalline addition compound with urea is known as **hyperol** and liberates hydrogen peroxide on solution in water.

Strength of hydrogen peroxide solution. The strength of aqueous solution of hydrogen peroxide is expressed in terms of volume in c.c. of oxygen evolved at N. T. P., when a unit volume of hydrogen peroxide solution is catalytically decomposed. Thus, if 1 c.c. of a hydrogen peroxide solution when decomposed, evolves 10 c.c. of oxygen at N. T. P., then that sample of hydrogen peroxide is of 10 volume strength. Similarly, 1 c.c. of 20 volume strength of a hydrogen peroxide solution when decomposed, yields 20 c.c. of oxygen at N. T. P. The relation between the volume strength and percentage strength of hydrogen peroxide can be established as follows :

$$\underset{(68 \text{ grams})}{2H_2O_2} = 2H_2O + \underset{(22{\cdot}4 \text{ litres at N. T. P.})}{O_2}$$

$\therefore$ 68 grams of hydrogen peroxide yield 22400 c.c. of oxygen at N. T. P.

$\therefore$ 1 gram of hydrogen peroxide yields 329·4 c.c. of oxygen at N. T. P.

Or, 100 c.c. of 1% solution of hydrogen peroxide yield 329·4 c.c. of oxygen at N. T. P.

$\therefore$ 1 c.c. of 1% solution of hydrogen-peroxide yields 3·294 c.c. of oxygen at N. T. P.

Hence, 1% solution of hydrogen peroxide is of 3·294 volume strength.

Therefore, 1 volume hydrogen peroxide is of $\frac{1}{3{\cdot}294}$ per cent strength. Or, 10 volume hydrogen peroxide is of $\frac{10}{3{\cdot}294} = 3{\cdot}04$ per cent strength.

Hence, a hydrogen peroxide solution of 'V' volume strength is of $\frac{V}{3{\cdot}294}$ per cent strength. Now, 1 (N) hydrogen peroxide solution is of 1·7 per cent strength* and hence 1 (N) hydrogen peroxide solution is of $1{\cdot}7 \times 3{\cdot}294 = 5{\cdot}6$ volume strength.

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* The equivalent weight of hydrogen peroxide is 17.

$\therefore$ 1000 c.c. of 1 (N) hydrogen peroxide solution contains 17 grams of hydrogen peroxide. Hence, 100 c.c. of 1 (N) hydrogen peroxide solution contains 1·7 grams of hydrogen peroxide. Hence, 1 (N) hydrogen peroxide solution is of 1·7 per cent strength.

Uses of hydrogen peroxide. The great importance of hydrogen peroxide lies in its use in one or more of the following capacities.

(i) **Mild antiseptic.** A 3% aqueous solution of hydrogen peroxide is applied to cuts or infections as mild antiseptic. It destroys some types of bacteria by oxidising them. It is also used as mouth-wash or gargle.

(ii) **Bleaching agent.** Because of the oxidising power of hydrogen peroxide, it is used to bleach cloth, hair, silk, straw, ivory, teeth and feathers. It is safer to use hydrogen peroxide on these materials than chlorine because water is the only by-product.

Darkened oil paintings can be brightened by washing with hydrogen peroxide solution.

(iii) **Fuel.** Hydrogen peroxide is used as a fuel in some rockets and airplanes. It is used for the combustion of other fuels such as alcohol, petrol and hydrazine hydrate. During world war II Germans used highly concentrated (about 90%) hydrogen peroxide as a source of oxygen for the combustion of fuels used in their jet propelled bombs and planes. It is also used alone in the reactor of a jet unit. When one pound of 90% hydrogen peroxide is decomposed by a catalyst in the reactor, it produces 60 cu. ft. of gas at 1300°F and one atmospheric pressure, which is shot out of the unit with enough velocity to drive a plane.

Highly concentrated (85 to 90 per cent) hydrogen peroxide is mixed with certain combustible substances to produce explosives.

(iv) **Antichlor.** Hydrogen peroxide is used as an antichlor to remove excess of chlorine from bleached fabrics.

(v) **Oxidising agent and reducing agent.** The solution of hydrogen peroxide is used as an oxidising agent in the dyeing industry and in the preparation of medicinals and pharmaceuticals. The solutions of hydrogen peroxide of different strengths are used in the laboratory as oxidising agents or reducing agents.

Tests for hydrogen peroxide. (i) Hydrogen peroxide liberates iodine from potassium iodide solution which forms a blue colouration with starch. Even a trace of hydrogen peroxide can be detected by a mixture of potassium iodide and ferrous sulphate ; ozone cannot liberate iodine from a mixture of potassium iodide and ferrous sulphate.

(ii) A solution of potassium dichromate acidified with sulphuric acid is added to a solution suspected to contain hydrogen peroxide. The resulting solution is rapidly shaken with ether. If the ethereal layer becomes deep blue in colour, then the solution contains hydrogen peroxide.

(iii) Titanium dioxide is heated with twice its volume of concentrated sulphuric acid ; the titanyl sulphate which results is cooled and diluted with water. A little of this solution is added to the liquid to be tested. If the hydrogen peroxide is present, an intense and stable orange yellow colour will develop. The colour is believed to be due to the formation of peroxytitanic acid.

APPENDIX

1. Distinctions of hydrogen peroxide from ozone

Hydrogen peroxide is distinguished from ozone by the following analytical tests :

Reagent	Ozone	Hydrogen peroxide
(1) (*a*) Potassium iodide solution.	Liberates iodine	Liberates iodine
(b) Potassium iodide + ferrous sulphate solution	Cannot liberate iodine.	Liberates iodine
(2) Mercury	Mercury loses mobility and forms a thin film on the glass.	No action.
(3) Silver	Silver is blackened.	No action.
(4) Filter paper soaked in alcoholic solution of benzidine.	Turns brown	No colour change.
(5) Filter paper soaked in alcoholic solution of tetramethyl base.	Turns violet	No colour change.
(6) Acidified solution of potassium dichromate + ether.	No characteristic change.	On shaking with hydrogen peroxide, ethereal layer becomes deep blue.
(7) Solution of titanyl sulphate.	No characteristic change.	An intense and stable orange yellow colouration is developed.
(8) Acidified potassium permanganate solution.	Pink colour is not discharged.	Pink colour is discharged.

II. A comparative study of ozone and hydrogen peroxide

	Ozone	Hydrogen Peroxide
(1)	It is an allotrope of oxygen.	It is a peroxide and has the structural formula H—O—O—H.
(2)	It is a pale blue gas having fishy smell.	It is a clear viscous liquid having smell like that of nitric acid.
(3)	It is a neutral gas.	It behaves like a dibasic acid.
(4)	It is soluble in water, carbon tetrachloride and turpentine oil.	It is soluble in water and ether.
(5)	It is an endothermic compound and unstable to heat and decomposes into oxygen. The decomposition is accompanied by the evolution of heat. The decomposition is catalysed by various substances.	It is less exothermic than water. It is thermally unstable and decomposes into water and oxygen. Certain substances act as positive catalysts and some substances act as negative catalysts in the decomposition reaction.
(6)	It is a strong oxidising agent.	It is also a strong oxidising agent.
(7)	It can act as reducing agent towards certain substances.	In reactions with strong oxidising agents, it behaves as a reducing agent.
(8)	It bleaches various substances by oxidation.	It also bleaches various substances by oxidation; it is also used as antichlor.
(9)	It kills various bacteria by oxidation.	It also kills various becteria by oxidation.
(10)	It forms addition compounds such as ethylene ozonide.	It also forms addition compounds such as $(NH_4)_2SO_4$, H_2O_2 and hyperol.

III. A comparative study of water and hydrogen peroxide.

Water	Hydrogen peroxide
It is an oxide and has the formula, H—O—H.	It is a peroxide and has the formula H—O—O—H.
It boils at 100°C under 760 mm pressure.	It boils at 151°C under 760 mm pressure.
It is a neutral liquid.	It behaves like a dibasic acid.
It is stable.	It is unstable.
It possesses neither oxidising nor reducing properties.	It possesses both oxidising and reducing properties.
It is an excellent solvent.	It fails to act as solvent.
It is not a bleaching agent.	It is a good bleaching agent.
It forms addition compounds such as $CuSO_4 . 5H_2O$, $FeSO_4 . 7H_2O$, etc.	It also forms addition compounds such as $(NH_4)_2SO_4 . H_2O_2$.

EXERCISES

1. How would you classify natural water according to sources? Mention the principal impurities which may be present in each class.

2. How is chemically pure water obtained from natural water? How would you purify a sample of water for drinking purpose?

3. What is meant by hardness of water? What are the causes of hardness? Describe various methods which are used for softening hard water. What are the disadvantages of hard water when used (a) in the laundry (b) in a boiler? [Bombay, '47]

4. How would you purify water for laboratory use? Explain the principles involved in ion-exchange or permutit method.

5. Describe briefly the properties of water and discuss its importance as solvent.

6. Compare the properties of water with those of hydrogen peroxide.

7. How would you test whether a given colourless liquid is or is not water?

8. Discuss the purification of water which is to be used for (a) drinking, (b) industrial and (c) laboratory work.

9. How and under what conditions does water react with the following substances?

(i) Sodium, (ii) Calcium, (iii) Magnesium, (iv) Aluminium, (v) Zinc, (vi) Iron, (vii) Sodium peroxide, (viii) Calcium oxide, (ix) Phosphorus trioxide, (x) Phosphorus pentoxide, (xi) Sulphur dioxide, (xii) Chlorine, (xiii) Calcium hydride and (xiv) Calcium carbide.

10. How would you prepare a solution of hydrogen peroxide? How would you prepare from this solution anhydrous hydrogen peroxide?

11. How is hydrogen peroxide prepared on a large scale? Give an account of its properties. "Hydrogen peroxide behaves both as an oxidising agent and as a reducing agent".—Discuss. [C. U. '33, '35]

12. Distinguish hydrogen peroxide from ozone. [C. U., '37]

13. What do you mean by "10 volume" hydrogen peroxide ? Calculate the strength of this solution in grams/litre.

14. You are given a gas that may be either oxygen or ozone. How would you identify it ? [C. U., '53]

15. Discuss the important uses of hydrogen peroxide.

16. "Hydrogen peroxide is a very strong oxidising agent"—Justify the statement. Upon what does the oxidising power of hydrogen peroxide depend ?

17. What is an auto-oxidation and reduction process ? "Hydrogen peroxide behaves both as an oxidising agent and a reducing agent"—Discuss.

18. What happens when

(a) hydrogen peroxide solution is treated with manganese dioxide.

(b) carbon dioxide gas is passed through a suspension of barium peroxide in water.

(c) hydrogen peroxide solution is added to acidified potassium iodide solution.

(d) hydrogen peroxide solution is gradually added to acidified potassium permanganate solution.

(e) hydrogen peroxide is treated with black lead sulphide.

(f) hydrogen peroxide is added (i) to acidified potassium ferrocyanide solution and (ii) to alkaline potassium ferricyanide solution.

(g) hydrogen peroxide solution is shaken with silver oxide.

(h) chlorine is passed through a solution of hydrogen peroxide.

19. Explain the following statements :

(i) Hydrogen peroxide manifests both oxidising and reducing properties.

(ii) Water does not possess oxidising property while hydrogen peroxide possesses oxidising properties.

(iii) Hydrogen peroxide acts as a diprotic acid.

(iv) Hard water is not used in laundry and in boilers.

(v) Water molecule is stable while hydrogen peroxide molecule is unstable.

20. Calculate in grams per litre the amount of hydrogen peroxide present in a sample of it which is of "20 volume strength".

[Ans. 60·8 gram/litre]

21. Calculate the strength in volume of hydrogen peroxide which is of 5 per cent strength.

[Ans. 16·47]

22. 5 c.c. of 0·15 (N) solution of hydrochloric acid are required to titrate 100 c.c. of water containing calcium bicarbonate. Calculate the hardness of water.

[**Solution** : Let the strength of water be x(N). Then $5\times0{\cdot}15(N)=x\times100$ whence $x=0{\cdot}0075$ (N) ∴ 1 litre of water contains 0·0075 gm-equivalent or, 7·5 mg-equiv. of calcium bicarbonate or 7·5 mg equiv. of calcium ions. The hardness of water is, therefore, 7·5 mg-equiv. per litre of water.

Now, 7·5 mg-equiv. of $Ca(HCO_3)_2 \equiv 7{\cdot}5$ mg-equiv. of $CaCO_3 \equiv 7{\cdot}5\times50$ mg of $CaCO_3$

∴ 1 litre of water contains 375 mg of $CaCO_3$. Hence, the hardness of water is 375 ppm or 37·5°.]

23. Calculate the temporary hardness of water in mg-equiv./litre and in degree knowing that 10 ml of a 0·05 (N) solution of hydrochloric acid were spent to react with the bicarbonate contained in 100 c.c. of water. [Ans. 5 mg equiv ; 25°]

24. Calculate the permanent hardness of water, knowing that 5·05 gm of anhydrous borax $Na_2B_4O_7$ were spent to remove calcium ions contained in 10 litres of water. [Ans. 25° or 250 ppm]

[**Hints** : $CaSO_4 + Na_2B_4O_7 = CaB_4O_7 + Na_2SO_4$]

25. One litre of a sample of hard water contains 1 mg of $CaCl_2$ and 1 mg of $MgCl_2$. Find the total hardness in terms of $CaCO_3$ per 10^6 parts of water by weight. [Ans. 1·95 ppm or 0·195°] [I.I.T., '80]

26. A sample of hard water contains 20 mg of Ca^{++} ions per litre. How many milliequivalents of Na_2CO_3 would be required to soften 1 litre of the sample ? [Ans. 1 milliequivalent] [I.I.T., '80]

27. The total hardness of a sample of water is 2·32 mg-equiv. per litre of water. How many grams of soda would be required to soften 20 litres of the sample ? [Ans. 2·46 gram]

28. The hardness of a sample of water is 10°. How many grams of soda should be added to 10 litres of this sample of water to remove its hardness ?

[**Solution** : 1 ppm ≡ 1 mg of $CaCO_3$ or its equivalent amount of other salts in 1 litre of water.

∴ 100 ppm ≡ 100 mg. of $CaCO_3$ or its equiv. amount of other salt in 1 litre of water.

∴ 10° ≡ 100 mg. of $CaCO_3$ or its equivalent amount of other salts in 1 litre of water.

∴ 10 litres of water whose hardness is 10° contain 1000 mg. of $CaCO_3$ or its equivalent amount of other salts.

∴ 10 litres of water whose hardness is 10° contain $\frac{1000}{50}$ mg.-equiv. of $CaCO_3$ or its equivalent amount of other salts. [50 is the equivalent weight of $CaCO_3$].

Hence, in order to remove the hardness, $\frac{1000}{50}$ mg-equiv. of Na_2CO_3 will be required. Now, the equivalent weight of Na_2CO_3 is 53.

∴ The quantity of soda which is required to remove the hardness $= \frac{1000}{50} \times 53$ mg. or 1060 mg. or 1·06 grams.]

CHAPTER IV

AIR

The mixture of gaseous substances which surrounds the earth is referred to as the atmosphere. The term air was applied by the older chemists to this gaseous mixture in the same sense as we use the word "gas". They regarded air as an element. The first reliable evidence of the composite nature of air was produced by Mayow (1674) who showed that the volume of air is diminished by the breathing of a mouse confined in a bell-jar over water. The same result occurs when combustible substances burned under similar conditions. The residual gases left after these experiments were unfit for further combustion or respiration. Black in 1755 discovered the presence of carbon dioxide in air and called it "fixed air". Having learned the isolation and identification of oxygen and nitrogen in air by Priestley and Scheele, Lavoisier in 1775 directed his attention to these discoveries and was led to the idea that air was a mixture of these two gases with moisture and carbon dioxide. The presence of inert gases, helium, neon, argon, krypton and xenon in air was discovered by Rayleigh more than a hundred years later.

Air is a mixture and not a compound. The following arguments show clearly that air is a mixture and not a chemical compound.

(1) The composition of air is not fixed but varies more or less from time to time and with the locality. For example, in a crowded room the percentage of carbon dioxide would be high and that of oxygen would be correspondingly reduced. Hence, the composition of air cannot be represented by a chemical formula. Since the composition of a chemical compound is fixed and invariable, the proportions of oxygen and nitrogen in air would be invariable if air were a compound of these two gases. Therefore, air is not a compound.

(2) When a compound is formed from two or more elements, there is a thermal change, i.e., heat is either evolved or absorbed, and often a volume change. But when nitrogen and oxygen are mixed together in the proportion in which they are present in air (four volumes of nitrogen and one volume of oxygen) there is no thermal change and no change in volume or colour. Thus, there is no sign of chemical reaction between the two gases. The mixture, however, behaves like an ordinary air in all respects except in so far as the properties of air are modified by the presence of other gases such as argon, carbon dioxide, etc.

(3) A chemical compound has its own characteristic properties and bears little, if any, resemblance to those of their constituents. The characteristic properties of air, on the other hand, are those that would be expected for a mixture of its components in the known proportions. This means that the constituents of air retain their original properties.

(4) There are 75·6 per cent of nitrogen and 23·1 per cent of oxygen by weight in air. Hence, if air were a compound, the ratio of the number of nitrogen and oxygen atoms in it would be

$$\frac{\text{number of atoms of nitrogen}}{\text{number of atoms of oxygen}}=\frac{75{\cdot}6/14}{23{\cdot}1/16}=\frac{5{\cdot}4}{1{\cdot}44}=\frac{15}{4}$$

On this basis, the simplest formula of air would be $N_{15}O_4$ (or a multiple of this) and hence its vapour density would be $274/2=137$. But, experimentally determined vapour density of air is 14·4. Therefore, air cannot be a compound.

The vapour density of air determined experimentally is in agreement with the value of vapour density calculated on the basis of the fact that air is a mixture of approximately 4 volumes of nitrogen and 1 volume of oxygen ; thus

$$5\times d=4\times 14+1\times 16$$
$$\therefore\ d=14.4$$

(where d is the vapour density of air ; 14 and 16 are the vapour densities of nitrogen and oxygen respectively)

(5) The constituents of air can be separated by means of physical processes such as (a) solution in water, (b) diffusion, (c) fractional distillation of liquid air, and (d) magnetic field.

(a) **By solution in water.** Oxygen is more soluble in water than nitrogen. Hence, when water is saturated with air, the dissolved air contains more oxygen than the undissolved air. When the solution is boiled, the air expelled contains 35 per cent of oxygen ; air contains only 21 per cent by volume of oxygen. Therefore, if air were a compound, its composition could not be altered in this way.

(b) **By diffusion.** When air is allowed to diffuse through a porous tube, nitrogen being lighter than oxygen, passes out more rapidly than oxygen. The diffused air is found to be richer in nitrogen than the undiffused air. Thus, air can be partially separated into its constituents.

(c) **By fractional distillation of liquid air.** When liquid air is distilled, the more volatile nitrogen distils off before oxygen. Hence, by distilling liquid air fractionally, air can be separated into its constituents. Had air been a chemical compound, it would have distilled as a whole.

(d) **By magnetic field.** When solidified air is subjected to a magnetic field, the highly paramagnetic oxygen is sucked out of *it* towards the magnet's poles. Thus, solid air behaves towards a magnet as a mixture of nitrogen and oxygen.

The constituents of the atmosphere and their functions. The composition of the atmosphere is complex. Its chief constituents can be divided into three groups :

(a) **Constant constituents.** Under this group are included the two major constituents, viz., oxygen (20·95% by volume) and nitrogen (78·09% by volume). Other members of this group are inert or noble gases (about 1% by volume), viz., argon, neon, helium, krypton and xenon. The content of these gases in air is practically the same everywhere.

(i) **Oxygen.** When nitric oxide, NO, which is a colourless gas is exposed to the air, it forms a reddish brown fumes due to the reaction of NO with oxygen. This proves that air contains free oxygen.

$$2NO+O_2=2NO_2.$$

When mercury is heated in air for a long time, red scales of mercuric oxide are obtained. On heating these red scales, oxygen is evolved.

$$Hg+air \rightarrow HgO$$
$$2HgO=2Hg+O_2$$

Thus, it is proved that atmosphere contains oxygen.

Living creatures require oxygen for respiration. They would not last more than a few minutes without oxygen. Oxygen breathed into the lungs oxidises the various complex organic substances of the body producing carbon dioxide which is exhaled. This process of oxidation is exothermic and living creatures derive their energy and warmth of the body from the heat evolved during such chemical processes. The presence of carbon dioxide in the air from lungs is easily demonstrated by blowing respired air into lime water which is turned milky. Human being, for example, inhales an average of 21% oxygen and 0·03% carbon dioxide and exhales 16% oxygen and 4% carbon dioxide.

Again, oxygen is essential for all types of combustion.

(ii) **Nitrogen.** The residual air which is left when phosphorus is burnt in a closed volume of air, does not support combustion and is readily absorbed by heated magnesium. Hence, air contains nitrogen.

Nitrogen dilutes oxygen, otherwise the process of combustion would be very rapid and the respiration would be dangerous for animal life.

(iii) **The inert gases.** The residual gas which remains when oxygen and nitrogen are removed from air by burning phosphorus and heated magnesium respectively, contains inert gases, argon, krypton, xenon, neon, helium and radon.

(b) **The variable constituents.** The group includes carbon dioxide (0·02—0·04%) and water vapour (up to 4%). The content of these constituents in the atmosphere vary depending on the various conditions.

(i) **Carbon dioxide.** When clear lime water is exposed to the atmosphere, a white crust is formed on its surface. This is due to the reaction of carbon dioxide present in air with lime water forming insoluble calcium carbonate.

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$$

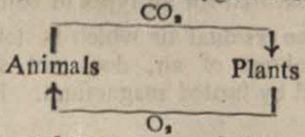
Oxygen-carbon dioxide cycle. Carbon dioxide is formed in nature due to the combustion of fuels such as coal, wood, etc., the respiration of the animals and the decay of vegetable and animal matters. The percentage of carbon dioxide is higher in towns than in the open country ; this is due to the fact that large quantities of the gas is discharged into the air by factories and plants in town, which burn large quantities of fuels. But diffusion of air by winds prevents the accumulation of excessive amount of the gas in any part of the globe. A large quantities of carbon dioxide also enter into the atmosphere by volcanic action in some parts of the globe.

Although enormous quantities of carbon dioxide enter into the atmosphere by the processes described above, the percentage of carbon dioxide in the atmosphere is relatively constant. This is due to a cyclic process ocurring in nature known as *oxygen-carbon dioxide cycle.*

Plants withdraw large quantities of carbon dioxide from air and convert it into carbohydrates (cellulose, starch and sugars) and oxygen. The energy required for converting carbon dioxide and water into carbohydrates and oxygen is obtained by the plants from sunlight. Such a process of carrying out a reaction by using the energy of sunlight is called photosynthesis :

$$6CO_2 + 6H_2O + \text{energy from sunlight} \rightarrow C_6H_{12}O_6 + 6O_2$$

Chlorophyll, the green colouring matter of the plant, acts as a catalyst. The vast quantities of oxygen released by plants enter into the atmosphere and support respiration of animals and combustion processes. Thus, the cycle of photosynthesis by plants and the respiration of animals and combustion processes continues indefinitely in the atmosphere and thus the percentage of carbon dioxide and oxygen in air is maintained constant.



Carbon dioxide is also removed from the atmosphere in the "weathering" of rocks such as felspars, which combine with atmospheric carbon dioxide to form soluble alkali carbonates.

$$K_2O, Al_2O_3, 6SiO_2+2H_2O+CO_2$$
$$=Al_2O_3, 2SiO_2, 2H_2O+4SiO_2+K_2CO_3$$

Carbon dioxide from air is also removed by sedimentary rocks such as limestone, $CaCO_3$, and dolomite, $MgCO_3$. These rocks react with carbon dioxide to form soluble bicarbonates which are carried by river water into oceans.

$$CaCO_3 + CO_2 + H_2O = Ca(HCO_3)_2$$
$$MgCO_3 + CO_2 + H_2O = Mg(HCO_3)_2$$

(ii) **Moisture.** When a watch glass containing fused calcium chloride is kept in air, calcium chloride becomes moist due to the absorption of water vapour present in air. The percentage of water vapour in air varies over a wide range, from a fraction of one per cent to several per cents. At least 10^5 tons of water vapour are usually present in the temperate region over each square mile of the earth's surface.

The dry air is heavier than the humid air since the average molecular weight of the gases in dry air is 29 while that of water vapour is only 18. Therefore, barometer always falls when the atmosphere acquires more than its usual content of water vapour.

When the air contains maximum amount of water vapour it can retain in contact with liquid water at a given temperature, it is said to be saturated at that temperature. The actual amount of aqueous vapour which air can carry before it is saturated depends upon the temperature. The higher the temperature, the greater amount of moisture it can carry. The pressure exerted by water vapour in fully saturated air is called the vapour pressure of water at that temperature.

At a given temperature, relative humidity is defined as the ratio of the quantity of moisture that air actually contains to what it would contain if it were fully saturated. Therefore, when air is fully saturated with water vapour, the humidity is 100 per cent. If a litre of air requires 17·1 mg of water vapour to become saturated at a given temperature, and if a litre of it actually contains 1·71 mg of water vapour, then the relative humidity is 10 per cent. The average humidity is about 66 per cent. There is much discomfort in a hot, humid day. This is due to the fact that the combination of high temperature and excessive humidity decreases the evaporation of perspiration from the skin. Ventilation or fanning hastens the evaporation of perspiration and thus affords relief.

The water vapour in the atmosphere controls the evaporation of water from the earth. Water vapour in air indirectly supports the lives of plant and animal, because rain is due to the presence of water vapour in the atmosphere. Water vapour, being only 0·62 times as heavy as an equal volume of air, rises into the upper regions of the atmosphere. The temperature of the ascending vapour gradually decreases, and consequently, a place is reached when air becomes completely saturated with water vapour. The water vapour then condenses into droplets as mist or clouds, and the condensed water ultimately descends to the earth in the form of rain, snow or hail.

(iii) **Dust particles.** Air contains noteworthy quantities of dust everywhere. Dust in air consists mainly of coal particles, particles of mineral substances, pollen grains from numerous flowering plants, and bacteria. The percentage of dust in air varies greatly ; it is generally higher in summer but lower in winter.

Bacteria enter into the atmosphere by wind current from soil went it is dry. Some of the bacteria are responsible for diseases but most of them are quite harmless. The dust particles to which bacteria cling, is most dangerous hygienically ; this is particularly true for the dust of dwellings which may carry infectious microbes, such as the tubercle bacillus. After a rain shower, the air contains but few bacteria because the rain drops carry the bacteria down with them.

(c) **Occasional constituents.** The presence of these constituents depends on the local conditions. Thus, in the vicinity of factories where sulphide ores are roasted, or coal containing sulphur is burned, the air contains sulphur dioxide ; it contains ammonia and hydrogen sulphide in the localities where organic remains are decomposing. Traces of ozone or hydrogen peroxide may also be present in air. Nitrogen oxides formed by the electrical discharges in the atmosphere may also be present. These impurities which are present in air in negligible quantities are continually removed from the air by the rain water which dissolves them.

The percentage composition of air can be expressed by the following figures, taking into account only the constant consituents :

	By volume	**By weight**
Nitrogen	78·16	75·5
Oxygen	20·9	23·2
Inter gases	0·94	1·3

Experimental methods of determining the composition of air. (a) **Composition of air by volume.** The volumetric composition of air can be determined by the following method :

Lavoisier's experiment. In 1773, Lavoisier performed experiments on the calcination of metals in a sealed vessel and found that only part of the air in the vessel is absorbed by the metals to form "calx" and the difference in the weight between the calx and the initial metal equals the weight of air absorbed. He showed that the part of air that disappears on combustion is oxygen and the gas which is left in the retort does not support combustion and was given by him the name "azote". Lavoisier's experiment with mercury is described below :

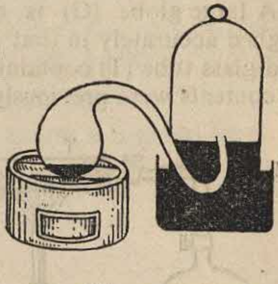


Fig. 4.1 : Lavoisier's experiment.

Lavoisier took a weighed quantity of mercury (4 ounces) in a glass retort, the neck of which was communicated with a measured volume of air in a bell-jar which was kept inverted over mercury (fig. 4.1). The volume of air in the bell-jar was noted. The retort was then heated by means of charcoal furnace for 12 days at a temperature near the boiling point of mercury. Red scales of mercury were formed on the surface of mercury in the retort. The volume of air in the bell-jar gradually decreased and consequently the level of mercury gradually rose up in the bell-jar during heating. After 12 days, the level of mercury was found to be steady. The residual gas in the bell-jar occupied about four-fifth of the volume of air originally taken and hence one-fifth of the volume of air was absorbed by mercury. The residual gas did not support respiration or combustion, and Lavoisier called this gas 'azote'. In France, the gas is still called 'azote' though in Britain it is called 'nitrogen'.

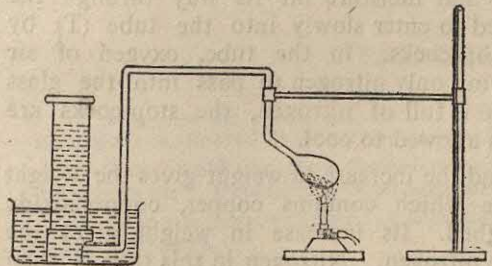


Fig. 4.2 : Lavoisier's experiment (Preparation of oxygen by heating mercuric oxide.).

Lavoisier next collected the 'red scales' and took them in a retort. The retort was then strongly heated when a gas was evolved which was collected in a graduated jar over mercury (fig. 4.2). The volume of the gas was found to be one-fifth of the volume of air taken in the bell-jar and was equal to the diminution of the volume of the air that took place when mercury was heated in the retort. This gas supported respiration and combustion. Lavoisier first called this gas the 'vital air' and afterwards 'oxygen'. When this gas was added to the azote, ordinary air was obtained. From these experiments, Lavoisier came to the following conclusions :

(i) Air is a mixture of two gases—oxygen and nitrogen. One-fifth of the air consists of oxygen and the remainder is nitrogen.

(ii) It is the oxygen of air which alone supports respiration and combustion, and combines with metals during calcination.

(b) **Composition of air by weight (Gravimetric composition). Dumas' method.** The composition of air by weight is determined by the method of Dumas.

A large globe (G) is evacuated, closed by a stop-cock, and weighed accurately in that condition. It is then attached to the hard glass tube (T) containing finely divided copper ; the tube and the contents were previously evacuated, closed by stop-cocks fitted at each end and weighed. The glass tube (T) at the other end is connected with a bulb of potash solution (X) and with two U-tubes, one (Y) containing solid caustic potash and the other (Z) containing fused calcium chloride.

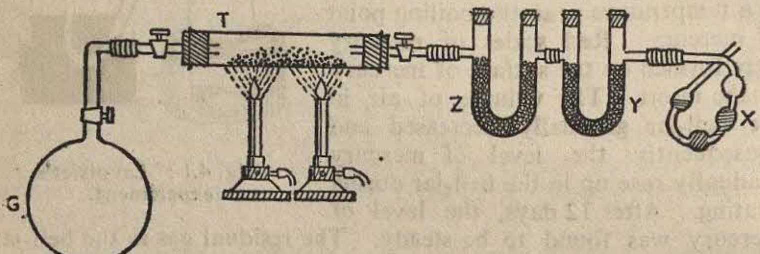


Fig. 4.3 : Dumas' experiment (Gravimetric composition of air).

The tube (T) is heated to bright redness and the air which is deprived of carbon dioxide and moisture on its way through the bulb and U-tubes, is allowed to enter slowly into the tube (T) by gradually opening the stop-cocks. In the tube, oxygen of air combines with copper, leaving only nitrogen to pass into the glass globe (G). When the globe is full of nitrogen, the stop-cocks are closed and the apparatus is allowed to cool.

The globe is weighed and the increase in weight gives the weight of nitrogen in it. The tube which contains copper, copper oxide and some nitrogen is weighed. Its increase in weight gives the weight of oxygen and some nitrogen. Nitrogen in this tube is then removed by a pump and the tube is weighed again, and the weight of nitrogen in the tube is determined. This weight of nitrogen must be added to the weight of nitrogen in the globe in order to find out the total weight of nitrogen. The weight of oxygen is obtained from the increase in weight of the glass tube after removing nitrogen.

Calculation. Let the weight of the vacuous globe $= W_1$ grams.
the weight of evacuated glass tube + copper $= W_2$ grams.
the weight of globe + nitrogen after the experiment $= W_3$ grams.
the weight of glass tube + copper + copper oxide + nitrogen $= W_4$ grams.
the weight of evacuated glass tube + copper + copper oxide $= W_5$ grams.

$\therefore$ Weight of nitrogen in the globe $= (W_3 - W_1)$ grams.
The weight of nitrogen in the glass tube $= (W_4 - W_5)$ grams.
Hence, the total weight of nitrogen $= (W_3 - W_1) + (W_4 - W_5)$ grams.
$= a$ grams (say)

Now, the weight of oxygen $= (W_5 - W_2)$ grams. $= b$ grams (say)
Therefore, the weight of air = weight of nitrogen + weight of oxygen.

$$= (W_3 - W_1) + (W_4 - W_5) + (W_5 - W_2)$$
$$= (a + b) \text{ grams.}$$

$$\therefore \text{ Percentage of oxygen} = \frac{b \times 100}{(a+b)}$$

$$\text{and percentage of nitrogen} = \frac{a \times 100}{(a+b)}$$

The following results are obtained by actual experiment :

Oxygen : Nitrogen = 22·92 : 77·08. Allowing for the presence of 0·933% by volume of argon, the composition of air freed from water vapour and carbon dioxide is now known to be 23·2% by weight of oxygen, 75·5% by weight of nitrogen and 1·3% by weight of argon, etc.

EXERCISES

1. What are the constituents of air ? Explain clearly how the composition of air is affected by plant and animal life.

2. How would you show the existence of oxygen, nitrogen and carbon dioxide in air ? Describe Lavoisier's experiment on the composition of air.

3. "Air is a mixture and not a compound." Give arguments in favour of this statement.

4. How would you prove that air and water contain a common constituent ? Give evidences to indicate that in one case the common constituent is chemically combined, while in the other it merely forms part of a mixture. [C. U., '51]

5. Describe at least two experiments to show that air contains approximately four volumes of nirogen and one volume of oxygen.

6. What is "oxygen-carbon dioxide" cycle ? How does it play an important role in the life of plants and animals ?

7. Describe with full experimental details the methods for determining the (a) proportions by volume of oxygen and nitrogen and (b) the proportions by weight of oxygen and nitrogen in the air.

8. Prove experimentally that (a) air contains oxygen ; (b) it is a mixture of oxygen and nitrogen and not a compound and (c) the ratio by volume of nitrogen and oxygen in air is 4 : 1. [H. S., '61, '63, '64 (Comp.)]

9. Why is a crust formed on lime water when kept exposed to air ? [H. S., '79]

10. The amount of oxygen in air should gradually decrease and that of carbon dioxide increase to a large extent as a result of the respiration of animals and various combustion processes taking place on the earth. Why does it not happen ? [H. S., '79]

11. One of the gases in air is a supporter of combustion ; the other is not—How would you prove this ? How would you prove the existence of CO_2 in air ?

CHAPTER V

THE NITROGEN AND ITS COMPOUNDS

NITROGEN

Atomic weight, 14·008 **Atomic number, 7**

Electronic configuration $1s^2\ 2s^2\ 2p^3$

Nitrogen occurs in the free state in air of which it contitutes 78% by volume or 75·5% by weight. It occurs also in combination, The principal inorganic nitrogen compounds which occur in nature are potassium nitrate, KNO_3, known as nitre or saltpetre and sodium nitrate, $NaNO_3$, known as chile saltpetre. Chile saltpetre occurs in thick deposits on the Pacific coast in Chile. Insignificant quantities of nitrogen, mainly as nitrates, are present in soils. It occurs in the body of every plant and animal as a constituent of complex organic compounds called proteins.

Preparation of nitrogen. Nitrogen may be prepared either (a) from air or (b) from compounds of nitrogen.

(a) **From air.** Nitrogen is prepared from air by removing oxygen by means of elements such as copper and phosphorus, which react easily with oxygen to form oxides. The processes of removing oxygen from air are described below.

(i) **By red-hot copper.** Air is first freed from carbon dioxide and moisture by passing it successively through strong caustic potash solution and concentrated sulphuric acid. It is then passed through a long tube containing copper turnings heated to bright redness. Oxygen of the air reacts with copper to form solid copper oxide :

$$2Cu + O_2 = 2CuO.$$

Nitrogen passes out and is collected by the displacement of water. Nitrogen thus obtained contains small quantities of inert gases such as argon, krypton, etc.

(ii) **By means of phosphorus.** A porcelain crucible containing a piece of phosphorus is floated on water in a trough. The crucible is covered with a graduated bell-jar which is fitted with a stopper. The level of water in the jar is noted. Now, the stopper is taken out, the phosphorus is kindled by a hot wire, and the stopper is quickly inserted. Phosphorus reacts with oxygen of the air to form dense white fumes of phosphorus pentoxide which dissolves in water :

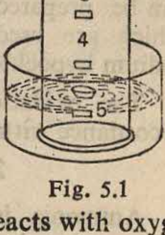


Fig. 5.1

$$P_4 + 5O_2 = 2P_2O_5$$

Water gradually rises up in the bell-jar and ultimately occupies one fifth of the volume occupied by air. The remaining four-fifths of the volume is occupied by the residual gas. That the residual gas is nitrogen is proved by its characteristic tests. This experiment proves that air is a mixture of 4 volumes of nitrogen and 1 volume of oxygen.

(iii) **By alkaline pyrogallate.** When air is passed through a solution of alkaline pyrogallate, oxygen of the air is absorbed while nitrogen remaining unabsorbed, passes out.

A flask containing alkaline pyrogallate solution is fitted with a stopper through which pass two glass tubes—one tube which dips into the solution serves as inlet for air. The other tube whose lower end remains above the surface of the solution serves as exit tube. The flask is connected to a U-tube containing soda lime and an aspirator completely filled with water. Water is then run slowly from the aspirator. Air is drawn through the flask where oxygen is absorbed and then through soda-lime tube where carbon dioxide is absorbed. Nitrogen of the air thus freed from oxygen and carbon dioxide collects in the aspirator.

(iv) A long glass tube sealed at one end is divided into six equal volumes by labels. A solution of cuprous chloride in conc. HCl is poured into it so as to occupy one volume. The tube is closed by a stopper and shaken thoroughly. Oxygen of the enclosed air is absorbed by cuprous chloride solution which becomes green in colour. When the tube is opened under water it is found that one of the remaining five divisions is filled with water and four-fifths of the original volume of air remain as nitrogen.

(v) On an industrial scale, nitrogen is obtained by the fractional distillation of liquid air. Nitrogen has a boiling point lower than that of oxygen ; hence it boils away more readily and is collected and compressed in steel cylinders.

(b) **From compounds of nitrogen.** (i) **From ammonia.** Nitrogen can be prepared by the oxidation of ammonia. Oxidising agents which are used for this purpose are cupric oxide, nitric oxide, sodium hypochlorite, bleaching powder and chlorine.

The oxidation of ammonia by cupric oxide takes place in accordance with the equation.

$$2NH_3+3CuO=3H_2O+3Cu+N_2$$

Ammonia is passed through a tube containing red-hot copper oxide. A mixture of steam and nitrogen is formed ; this mixture is passed through conc. H_2SO_4 which absorbs water, and dry nitrogen is finally collected over mercury.

Very pure nitrogen is obtained when a mixture of nitric oxide and ammonia in the correct proportion is passed over red-hot copper gauze. The reaction takes place in accordance with the equation.

$$4NH_3 + 6NO = 5N_2 + 6H_2O$$

Steam is removed by passing the mixture through conc. H_2SO_4 and finally pure and dry nitrogen is collected over mercury.

When a paste of bleaching powder is warmed with concentrated solution of ammonia, nitrogen is evolved.

$$2NH_3 + 3Ca(OCl)Cl = 3CaCl_2 + 3H_2O + N_2$$

Nitrogen may be prepared by adding sodium hypobromite solution drop by drop into concentrated ammonia solution.

$$2NH_3 + 3NaOBr = 3NaBr + 3H_2O + N_2$$

When chlorine gas is passed into a strong solution of ammonia in water, nitrogen is evolved.

$$2NH \;+ 3Cl_2 = 6HCl + N_2$$
$$HCl + NH_3 = NH_4Cl$$

The preparation must be stopped while there is still an excess of ammonia, as a further reaction between chlorine and the ammonia solution will lead to the formation of dangerously explosive nitrogen trichloride, NCl_3.

(ii) **From nitric acid.** Nitric acid vapour is passed through a tube containing strongly heated metallic copper. Under this condition, nitric acid reacts with copper, evolving nitrogen. The gas is passed through strong caustic potash solution which removes unreacted nitric acid vapour and is then collected over water.

$$5Cu + 2HNO_3 = 5CuO + H_2O + N_2$$

(iii) **From ammonium dichromate.** When red crystals of ammonium dichromate or a mixture of ammonium chloride and potassium dichromate is heated, nitrogen and steam are evolved. Ammonium dichromate decomposes violently with flashes of light.

$$(NH_4)_2Cr_2O_7 = N_2 + 4H_2O + Cr_2O_3$$

Steam is removed by passing the mixture through conc. H_2SO_4, and nitrogen is then collected by the displacement of mercury.

(iv) **From barium azide.** Very pure nitrogen is obtained by heating barium azide in vacuo.

$$Ba(N_3)_2 = Ba + 3N_2$$

(v) **From ammonium nitrite. Laboratory preparation.** In the laboratory, nitrogen is prepared in moderate quantities by the pyrolytic decomposition of ammonium nitrite.

$$NH_4NO_2 = 2H_2O + N_2$$

Since this salt is very unstable and expensive, the same reaction is usually brought about by heating a mixture of sodium nitrite and ammonium chloride.

$$\begin{array}{l} \mathrm{NaNO_2+NH_4Cl=NaCl+NH_4NO_2} \\ \mathrm{NH_4NO_2} \qquad \mathrm{=N_2 \; +2H_2O} \\ \hline \mathrm{NaNO_2+NH_4Cl=NaCl+2H_2O+N_2} \end{array}$$

Procedure. A concentrated solution of equimolecular amounts of sodium nitrite and ammonium chloride in water is taken in a round bottomed flask fitted with a thistle funnel and a delivery tube. The end of the thistle funnel should dip under the surface of the solution in the flask. The end of the delivery tube is introduced into a gas-jar which is filled with water and kept inverted under water in a trough. The flask is now gently heated and as soon as nitrogen begins to be evolved, the source of heat is removed. The gas is collected by the displacement of water in which it is only very sparingly soluble.

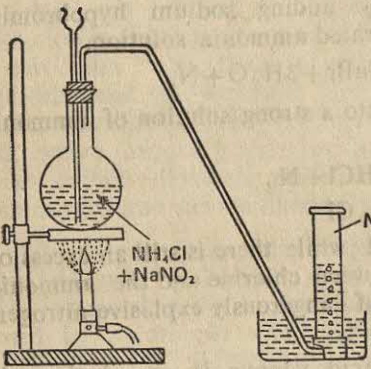


Fig. 5.2

The gas thus obtained contains traces of chlorine, ammonia nitric oxide, and moisture. The gas is purified by passing it successively (i) through alkali solution to remove traces of chlorine, (ii) through concentrated sulphuric acid to remove moisture and ammonia, and (iii) then over heated copper to remove oxides of nitrogen. The gas is finally collected over mercury.

Nitrogen prepared from compounds is free from inert gases and is known as *chemical nitrogen.*

The nitrogen obtained from air contains small amount of inert gases like argon, krypton, xenon, etc., each of which is heavier than nitrogen. For this reason, nitrogen obtained from air is slightly heavier than chemical nitrogen. The density of nitrogen obtained from air is 1·2572 and that of chemical nitrogen is 1·2505.

Properties of nitrogen. (A) Physical properties. Nitrogen is a colourless, odourless gas. It is slightly soluble in water and is little lighter than air. The nitrogen molecule is diatomic. The gas does not support combustion or respiration.

When cooled strongly under high pressure, nitrogen condenses to a colourless liquid which boils at $-195{\cdot}8$°C and solidifies to a white snow-like mass melting at -210°C.

(B) **Chemical properties:** (i) **Thermal dissociation.** The molecules of nitrogen are peculiarly stable. It dissociates into atoms only at very high temperature; only 5 per cent of the nitrogen is dissociated at 3500°C.

$$N_2 + 172{,}000 \text{ cal} \rightleftharpoons 2N$$

Because of this stability and high dissociation energy, nitrogen shows slight chemical activity; conversely, its compounds possess great chemical activity. For this reason, the compounds of nitrogen are the most important of chemical substances.

At ordinary temperatures, nitrogen is incapable of forming compounds but at high temperatures it reacts quite readily with certain substances.

(ii) **Reaction with metals.** At high temperatures, nitrogen combines directly with certain metals such as lithium, calcium, boron and magnesium to form nitrides.

$$6Li + N_2 = 2Li_3N \text{ (lithium nitride)}$$

$$3Ca + N_2 = Ca_3N_2 \text{ (calcium nitride)}$$

$$3Mg + N_2 = Mg_3N_2 \text{ (magnesium nitride)}$$

These nitrides are decomposed by water with the formation of ammonia and metallic hydroxide.

$$Ca_3N_2 + 6H{\cdot}OH = 3Ca(OH)_2 + 2NH_3$$

$$Mg_3N_2 + 6H{\cdot}OH = 3Mg(OH)_2 + 2NH_3$$

(iii) **Reaction with non-metals.** Nitrogen combines directly with hydrogen to form ammonia under the influence of electric spark. Under a pressure of 200 atmospheres and in the presence of a suitable catalyst, nitrogen also combines directly with hydrogen at 500°C to form ammonia. This process is used for preparing ammonia on an industrial scale.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

Nitrogen does not burn in oxygen, but when a mixture of nitrogen and oxygen is passed through a powerful electric arc, nitric oxide is formed.

$$N_2 + O_2 \rightleftharpoons 2NO$$

Nitrogen does not directly combine with halogens.

(iv) **Reaction with compounds.** When calcium carbide is heated to about 1100°C in an atmosphere of nitrogen, calcium cyanamide is formed. Calcium cyanamide is commercially known as "nitrolim" and is used as a nitrogenous fertiliser.

$$CaC_2 + N_2 = CaCN_2 + C$$

Calcium cyanamide is decomposed by steam forming ammonia.

$$CaCN_2 + 3H_2O = CaCO_3 + 2NH_3$$

Active Nitrogen. When nitrogen at very low pressures is subjected to an electric discharge in a tube, an unusual form of nitrogen appears. The gas continues to emit a yellow glow for several hours after the discharge has been stopped. At the same time, the chemical properties of the gas are changed ; it becomes more reactive than ordinary nitrogen. It combines directly at low temperatures, with sulphur, iodine and phosphorus, and with many metals. It also reacts with acetylene forming hydrocyanic acid.

$$C_2H_2 + 2N = 2HCN$$

It also reacts with other organic compounds. It reacts with nitric oxide to form nitrogen dioxide.

$$2NO + N = NO_2 + N_2$$

This unusual form of nitrogen is called **active nitrogen.** The production of active nitrogen is catalysed by the presence of traces of impurities such as oxygen, mercury vapour or certain other substances.

The nature of active nitrogen has been the subject of much discussion. It is thought at present that the unusual reactivity of active nitrogen is due to the presence of free atoms and energetically excited nitrogen molecules.

Uses of nitrogen. (i) Large quantities of nitrogen are used for the production of nitrogen compounds, notably ammonia. The major use of nitrogen compounds is as fertiliser. (ii) Light bulbs are filled with nitrogen to retard the evaporation of the white-hot filament.

(iii) Nitrogen is used to provide an inert atmosphere for certain metallurgical operations.

(iv) Liquid nitrogen is used as a refrigerating agent.

Detection of nitrogen. Because of its inertness at ordinary temperature, nitrogen is usually identified in a negative way, i.e., by its lack of response to tests for other gases. The gas is usually confirmed by passing it over heated magnesium and treating the product with water. The formation of ammonia indicates the presence of nitrogen in the original gas.

Compounds of Nitrogen

Hydrides of nitrogen. Nitrogen forms several compounds with hydrogen. In these compounds, the average oxidation number of nitrogen ranges from $-\frac{1}{3}$ to -3. Three of these compounds are shown in table 5.1.

Table 5.1

Name	Formula	Oxidation state of nitrogen
Ammonia	NH_3	-3
Hydrazine	N_2H_4	-2
Hydrazoic acid	HN_3	$-\frac{1}{3}$

AMMONIA

Ammonium chloride, NH_4Cl. called sal-ammoniac was first prepared in Egypt from the "soot" obtained by burning camel's dung. In 1774, Priestley obtained the ammonia gas by heating lime with sal-ammoniac in a retort and collecting it over mercury. He called it the "alkaline air". The formula, NH_3, was established by Davy (1800) and Henry (1809).

Traces of ammonia occur in atmospheric air and in natural water. It is produced by the action of putrefying bacteria on organic matter present in soil. In stable, the urea from the urine of animals is converted into ammonium carbonate by the action of bacteria : ammonium carbonate then slowly decomposes into ammonia and carbon dioxide.

$$CO(NH_2)_2+2H_2O=(NH_4)_2CO_3$$
$$(NH_4)_2CO_3=2NH_3+H_2O+CO_2$$

Hence, odour of ammonia is often detected near stables. Ammonium sulphate, $(NH_4)_2SO_4$, and ammonium chloride, NH_4Cl, are found to occur in volcanic districts.

Preparation of ammonia. Ammonia can be prepared by the following methods :

(i) **From oxygen compounds of nitrogen.** (a) Ammonia can be obtained by the reduction of some oxides of nitrogen. When a mixture of hydrogen and nitric oxide or a higher oxide of nitrogen (except nitrous oxide) is passed over heated platinum, ammonia is obtained.

$$2NO+5H_2=2NH_3+2H_2O$$
$$2NO_2+7H_2=2NH_3+4H_2O$$

(b) Pure ammonia is obtained when sodium nitrate or sodium nitrite is heated with a solution of caustic soda and zinc or aluminium. Nascent hydrogen formed by the action of zinc or aluminium on alkali reduces sodium nitrate or nitrite.

$$Zn+2NaOH=Zn(ONa)_2+2H$$
$$NaNO_3+8H=NaOH+2H_2O+NH_3$$
$$NaNO_2+6H=NaOH+H_2O+NH_3$$

(ii) **From metallic nitrides.** Nitrides of active metals are decomposed by water to give ammonia.

$$Mg_3N_2 + 6H_2O = 3Mg(OH)_2 + 2NH_3$$
$$AlN + 3H_2O = Al(OH)_3 + NH_3$$

Calcium cyanamide reacts with water to form ammonia.

$$CaCN_2 + 3H_2O = CaCO_3 + 2NH_3$$

(iii) **From ammonium salts. Laboratory preparation of ammonia.** Ammonia can be prepared by heating an ammonium salt with a strong base. In the laboratory, it is usually prepared by heating a mixture of ammonium chloride and dry slaked lime. The reaction is represented by the equation.

$$2NH_4Cl + Ca(OH)_2 = CaCl_2 + 2H_2O + 2NH_3$$

Water vapour is evolved along with ammonia.

An intimate mixture of ammonium chloride (one part) and dry slaked lime (three parts) is taken into a flask. The flask is then heated and the evolved ammonia is passed through a tower (T) containing lumps of quicklime, CaO, which combines with water vapour to form calcium hydroxide, $Ca(OH)_2$.

$$CaO + H_2O = Ca(OH)_2$$

The gas thus dried is collected by the downward displacement of air. It can also be collected over mercury. It cannot be collected over water because the gas is highly soluble in it.

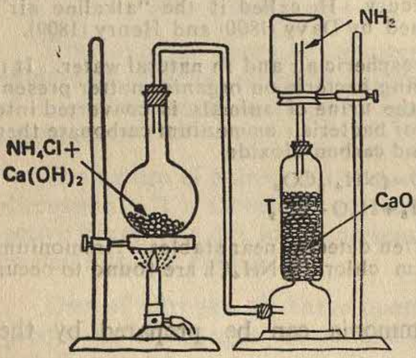


Fig. 5.3

Drying of ammonia. The gas cannot be dried by ordinary drying agents such as concentrated sulphuric acid, phosphorus pentoxide and calcium chloride since these substances readily react with ammonia. Thus, sulphuric acid reacts with ammonia to form ammonium sulphate.

$$H_2SO_4 + 2NH_3 = (NH_4)_2SO_4$$

Phosphorus pentoxide in presence of water vapour reacts with it to form ammonium phosphate.

$$P_2O_5 + 3H_2O + 6NH_3 = 2(NH_4)_3PO_4$$

Calcium chloride also absorbs ammonia to form the compound, $CaCl_2, 8NH_3$. Ammonia is usually dried by quicklime.

Properties of ammonia. (A) Physical properties : Ammonia is a colourless gas with pungent smell. It is lighter than air and can be easily condensed to a colourless liquid which boils at −33·4°C and freezes at −77·7°C. Like water, liquid ammonia is a bad conductor of heat and electricity, but it is an excellent solvent for many electrolytes.

The gas is extremely soluble in water—one volume of water absorbs about 1200 volumes of ammonia at N. T. P. The aqueous solution of the gas is alkaline. A concentrated solution of ammonia is known as **liquor ammonia fortis.** The solubility of ammonia gas may be demonstrated by the fountain experiment.

A large dry round bottomed flask is filled with ammonia by the displacement of air and fitted with a rubber stopper through which pass a long glass tube ending in a jet inside the flask and a dropper. The flask is inverted with the tube dipping in water in a beaker (fig. 5.4). A few drops of water are introduced into the flask by means of the dropper. The water dissolves some of the ammonia gas, creating a partial vacuum which permits water from the beaker to be forced upward by the atmospheric pressure into the flask. Water rushes out of the jet like a fountain until the flask is full.

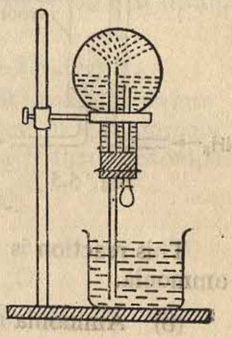


Fig. 5.4

(B) **Chemical properties :** Ammonia is chemically active and is used widely in both the gaseous and liquid states.

(i) **Thermal stability.** Ammonia is not very stable to heat and decomposes into its elements almost completely at 700°C.

$$2NH_3 \rightleftharpoons N_2 + 3H_2$$

(ii) **Reaction with active metals.** When ammonia gas is passed over heated sodium or potassium, hydrogen is liberated and sodamide or potassamide is formed. In this reaction, hydrogen is displaced by a metal and ammonia gas displays acid rather than basic properties.

$$2Na + 2NH_3 = 2NaNH_2 + H_2$$
$$2K + 2NH_3 = 2KNH_2 + H_2$$

Sodamide or potassamide is hydrolysed by water forming ammonia and caustic soda or caustic potash.

$$NaNH_2 + H_2O = NH_3 + NaOH$$
$$KNH_2 + H_2O = KOH + NH_3$$

However, when magnesium is heated in ammonia gas, magnesium nitride is formed.

$$3Mg + 2NH_3 = Mg_3N_2 + 3H_2$$

Similarly, with lithium, lithium nitride is formed.

$$6Li + 2NH_3 = 2Li_3N + 3H_2$$

(iii) **Reaction with non-metals.** (a) Ammonia does not readily burn in air, but burns in oxygen with a yellow flame, forming water and nitrogen. A mixture of ammonia and oxygen explodes when kindled. The ability of ammonia to burn in oxygen is due to its instability towards heat :

$$\begin{aligned} 4NH_3 &= 2N_2 + 6H_2 \\ 6H_2 + 3O_2 &= 6H_2O \\ \hline 4NH_3 + 3O_2 &= 2N_2 + 6H_2O \end{aligned}$$

When a mixture of ammonia and air is passed over a platinum gauze heated to 500°C, ammonia is oxidised to nitric oxide.

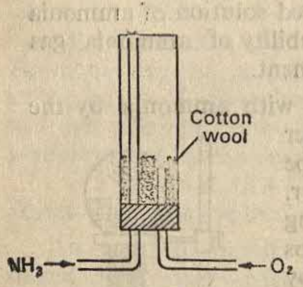


Fig. 5.5

$$4NH_3 + 5O_2 = 4NO + 6H_2O$$

This reaction is employed in the manufacture of nitric acid from ammonia.

(b) Ammonia reacts with chlorine ; ammonium trichloride and hydrochloric acid are formed if chlorine is in excess

$$NH_3 + 3Cl_2 = NCl_3 + 3HCl$$

Nitrogen trichloride is an oily liquid which decomposes into its elements with violent explosion on heating above 90°C (or on percussion).

When ammonia is in excess, chlorine merely removes hydrogen and liberates nitrogen.

$$\begin{aligned} 2NH_3 + 3Cl_2 &= N_2 + 6HCl \\ 6HCl + 6NH_3 &= 6NH_4Cl \\ \hline 8NH_3 + 3Cl_2 &= N_2 + 6NH_4Cl \end{aligned}$$

Bromine reacts with ammonia in a similar manner.

When a concentrated solution of ammonia is treated with iodine, a dark brown precipitate of nitrogen iodide is formed. The dark brown precipitate is a mixture of NI_3 with NHI_2 and NH_2I. Nitrogen iodide is extremely unstable and explodes, when dry, at the slightest touch.

Ammonia is oxidised by bleaching powder to nitrogen.

$$3Ca(OCl)Cl + 2NH_3 = 3CaCl_2 + 3H_2O + N_2$$

(iv) **Reaction with compounds.** (a) **Reducing property.** Ammonia gas, because of its instability to heat, is an excellent reducing agent and will free a number of metals from their oxides. Thus, when a stream of the gas is passed over cupric oxide heated in a hard glass tube, copper oxide is reduced to copper and ammonia is oxidised to nitrogen.

$$\begin{aligned} 2NH_3 &= N_2 + 3H_2 \\ 3CuO + 3H_2 &= 3Cu + 3H_2O \\ \hline 2NH_3 + 3CuO &= N_2 + 3Cu + 3H_2O \end{aligned}$$

Lead monoxide is reduced by ammonia to lead.

$$3PbO + 2NH_3 = 3Pb + N_2 + 3H_2O$$

Similarly, ammonia reduces potassium permanganate at ordinary temperatures.

$$2NH_3 + 2KMnO_4 = 2KOH + 2MnO_2 + 2H_2O + N_2$$

(b) **Reaction with carbon dioxide.** When 2 volumes of ammonia gas and 1 volume of carbon dioxide are mixed, ammonium carbamate is produced ; ammonium carbamate then decomposes to urea and water.

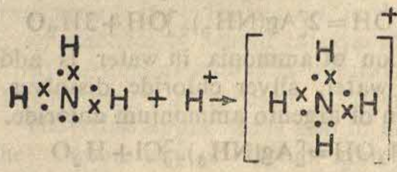
$$2NH_3 + CO_2 \rightleftharpoons \underset{\text{(ammonium carbamate)}}{NH_2{\cdot}CO{\cdot}ONH_4}$$

$$NH_2CO.ONH_4 = CO(NH_2)_2 + H_2O$$

In presence of water, ammonia reacts with carbon dioxide to form ammonium carbonate.

$$2NH_3 + CO_2 + H_2O = (NH_4)_2CO_3$$

(c) **Addition.** In the ammonia molecule, three out of five outermost electrons of nitrogen atom are shared with three hydrogen atoms ; a pair of electrons remains unshared. Hence, the ammonia molecule forms co-ordinate covalent unions with a number of ions and molecules which can accept a pair of electrons. Thus, with acids it reacts to form ammonium salts in which the ammonium radical, NH_4^+, plays the part of a positively charged univalent metal ion. It combines directly with hydrochloric and sulphuric acids to form ammonium chloride and ammonium sulphate :



$$NH_3 + HCl = NH_4Cl$$

$$2NH_3 + H_2SO_4 = (NH_4)_2SO_4$$

Ammonia also adds to di- and trioxide of sulphur and boron trifluoride :

$$NH_3 + BF_3 = H_3N{\rightarrow}BF_3$$

When dissolved in water, ammonia partially forms ammonium hydroxide. Ammonium hydroxide dissociates partially into NH_4^+ ion and OH^- ion.

$$NH_3+H_2O \rightleftharpoons NH_4OH \rightleftharpoons NH_4^++OH^-$$

The solution of ammonia in water feel and taste soapy and act weakly basic. It precipitates many metallic hydroxides from solutions of their salts.

$$FeCl_3+3NH_4OH=Fe(OH)_3+3NH_4Cl$$
$$ZnCl_2+2NH_4OH=Zn(OH)_2+2NH_4Cl$$
$$AlCl_3+3NH_4OH=Al(OH)_3+3NH_4Cl$$

Upon neutralisation with acids, solutions of ammonia yield ammonium salts. Because of these properties, it is thought that there are established hydrogen bonds between ammonia and water dipoles.

(d) Anhydrous calcium chloride, zinc chloride, etc., form addition compounds with ammonia, viz., $CaCl_2$, $8NH_3$; $ZnCl_2$, $8NH_3$.

Complex compound formation. Ammonia combines with many metallic ions because of the ability of the nitrogen atom in ammonia to share its unused pair of electrons to form complex ions.

(i) When a solution of ammonia in water (NH_4OH) is added to copper sulphate solution a pale blue precipitate of basic copper sulphate is first formed. This redissolves in excess of ammonia because of the formation of the complex cuprammoniun hydroxide.

$$^*2CuSO_4+2NH_4OH=CuSO_4,\ Cu(OH)_2+(NH_4)_2SO_4$$
$$CuSO_4,\ Cu(OH)_2+(NH_4)_2SO_4+6NH_4OH$$
$$=2[Cu(NH_3)_4]SO_4+8H_2O.$$

(ii) When ammonium hydroxide is added to silver nitrate solution, precipitate of silver oxide is first formed. On adding excess of ammonium hydroxide, the precipitate dissolves forming argento ammonium hydroxide.

$$2AgNO_3+2NH_4OH=Ag_2O+H_2O+2NH_4NO_3$$
$$Ag_2O+4NH_4OH=2[Ag(NH_3)_2]OH+3H_2O$$

(iii) When a solution of ammonia in water is added to silver chloride suspended in water, silver chloride dissolves completely forming a clear solution of argento ammonium chloride.

$$^{**}AgCl+2NH_4OH=[Ag(NH_3)_2]Cl+H_2O$$

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* **Explanation :** $CuSO_4+2NH_4OH=Cu(OH)_2+(NH_4)_2SO_4$
$Cu(OH)_2 \rightleftharpoons Cu^{++}+2OH^-$
$Cu^{++}+4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{++}$

** **Explanation :** $AgCl \rightleftharpoons Ag^++Cl^-$
$2NH_4OH=(2NH_3+2H_2O)$
$Ag^++2NH_3=[Ag(NH_3)_2]^+$

(iv) When ammonium hydroxide is added to a solution of zinc sulphate or zinc chloride, white precipitates of zinc hydroxide is first formed. This redissolves in excess of ammonia because of the formation of soluble zinc tetramino hydroxide.

$$^{*}ZnSO_4+2NH_4OH=Zn(OH)_2+(NH_4)_2SO_4$$

$$Zn(OH)_2+4NH_4OH=[Zn(NH_3)_4](OH)_2+4H_2O$$

(v) When ammonium hydroxide is added to the solution of mercuric chloride, white precipitates of amminomercuric chloride are formed.

$$HgCl_2+2NH_4OH=Hg(NH_2)Cl+NH_4Cl+2H_2O$$

(vi) When mercurous chloride comes in contact with ammonia, it blackens due to the separation of particles of mercury.

$$Hg_2Cl_2+2NH_4OH=Hg(NH_2)Cl+Hg+NH_4Cl+2H_2O$$

Uses of ammonia. (i) Almost all industrial ammonia is used in the production of other nitrogen compounds. Fertilisers such as ammonium sulphate, ammonium phosphate, urea and nitro-chalk (one part $CaCO_3$ to one part NH_4NO_3 by weight) are manufactured from ammonia. Nitric acid, nitrates and nitrites are also extensively manufactured by processes which depend upon the aerial oxidation of ammonia to oxides of nitrogen (Ostwald process). Ammonia is also consumed in the manufacture of sodium carbonate by Solvay process.

Ammonium nitrate is an important explosive and is commonly used in conjunction with picric acid for filling shells. It is also a component of many kinds of dynamite. Ammonium chloride, NH_4Cl, is used in dry cells, in dyeing industry, in textile printing, and in soldering and tin plating. The action of ammonium chloride in soldering is due to the fact that ammonium chloride when heated decomposes into ammonia and hydrochloric acid. Hydrochloric acid dissolves metal oxides forming metal chlorides which volatilise away. The metal surface thus becomes clean and the solder adheres well to the clean surface.

(ii) Liquid ammonia is used as an industrial source of hydrogen. It is transported in cylinders and is then decomposed into its elements by an electrically heated catalyst to give a cheap supply of hydrogen. (iii) Aqueous ammonia solution is used as a reagent in chemical laboratories. It is used in chemical plants as weak volatile base. They find applications also in medicine and in home. (iv) Since the evaporation of liquid ammonia is accompanied by the absorption of a large amount of heat (327 cal. per gram), liquid ammonia is used as a refrigerant.

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* **Explanation :** $ZnSO_4+2NH_4OH=Zn(OH)_2+(NH_4)_2SO_4$

$$Zn(OH)_2\rightleftharpoons Zn^{++}+2OH^-$$

$$4NH_4^{+}OH=(4NH_3+4H_2O)$$

$$Zn^{++}+4NH_3=[Zn(NH_3)_4]^{++}$$

Detection and estimation of ammonia. Ammonia is detected qualitatively by the following tests : (i) It is characterised by its pungent smell and its action on litmus paper (it turns red litmus paper blue). (ii) It forms dense white fumes with gaseous hydrogen chloride. (iii) Ammonia gas blackens a strip of paper moistened with mercurous nitrate solution. (iv) The presence of traces of ammonia or ammonium salts in water is detected by the addition of **Nessler's reagent** (it is an alkaline solution of potassium mercuric iodide, K_2HgI_4 prepared by adding potassium iodide to a solution of mercuric salt till the precipitate first formed redissolves). A yellow to orange yellow colouration or a precipitate is obtained. This is the most sensitive test for ammonia and ammonium salts.

Ammonia is estimated by titration against a standardised acid using methyl orange as indicator. The ammonia in ammonium salts is estimated by distilling the salt with excess of sodium hydroxide and passing the distillate into a known volume of standard acid. The excess of acid is then estimated by titrating it with standard alkali. The amount of ammonia contained in ammonium salts can be then calculated.

Ammonium salts. Ammonia is a weak base, but it can be neutralised by acids. If the neutralised ammonia solutions are evaporated, solid crystalline substances separate out. These substances which possess all the properties of typical salts are called ammonium salts. Ammonium salts can be formed not only by neutralising aqueous ammonia solutions but also by direct union between gaseous ammonia and anhydrous acids. For example :

$$NH_3+HCl=NH_4Cl.$$

Most of the ammonium salts are white crystalline solids which are ionic in character. They are soluble in water in which they behave as strong electrolyte. In solution, they dissociate completely into ammonium ion, NH_4^+ and a negative ion. Thus ammonium chloride when dissolved in water, dissociates as

$$NH_4Cl\rightleftharpoons NH_4^++Cl^-$$

The ammonium ion, NH_4^+, is a compound positive ion which closely resembles the ion of alkali metal, potassium. Hence, the ammonium salts are often very similar to and isomorphous with the corresponding salts of alkali metals, particularly potassium. The chief points of difference are the volatility and the instability of ammonium salts upon being heated and their decomposition into ammonia when warmed with a base. When heated, ammonium salts dissociate quite readily into ammonia and an acid. For instance :

$$NH_4Cl\rightleftharpoons NH_3+HCl$$

Among the ammonium salts only nitrate and nitrite do not undergo dissociation, but decompose when strongly heated. Thus,

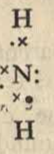
$$NH_4NO_3 = N_2O + 2H_2O \; ; \; NH_4NO_2 = N_2 + 2H_2O$$

When an aqueous solution of ammonium salts is treated with an alkali, ammonia is evolved :

$$(NH_4)_2SO_4 + 2NaOH = Na_2SO_4 + 2NH_3 + 2H_2O$$

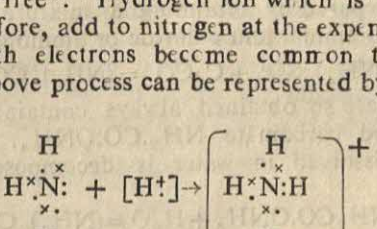
Numerous attempts to isolate NH_4 as a neutral entity have failed. Free ammonium should have possessed the properties of a metal. Its metallic nature is shown by the formation of an unstable ammonium amalgam which is very much like the amalgams of the alkali metals.

The formation of ammonium ions as a result of the reaction between ammonia and acids or water is due to the structure of ammonia molecule which can be represented as follows :



$$\begin{array}{c}\mathrm{H}\\ \cdot\times\\ \mathrm{H}^{\times}_{\cdot}\mathrm{N}:\\ \times\bullet\\ \mathrm{H}\end{array}$$

Thus, out of five electrons of nitrogen available for sharing, three electrons form pairs with hydrogen electrons and a pair of electrons remains "free". Hydrogen ion which is deprived of its electron can, therefore, add to nitrogen at the expense of this pair ; after addition, both electrons become common to nitrogen and hydrogen. The above process can be represented by the following scheme :



$$\begin{array}{c}\mathrm{H}\\ \cdot\times\\ \mathrm{H}^{\times}_{\cdot}\mathrm{N}:\\ \times\cdot\\ \mathrm{H}\end{array} + [\mathrm{H}^{+}] \rightarrow \left[\begin{array}{c}\mathrm{H}\\ \cdot\times\\ \mathrm{H}^{\times}_{\cdot}\mathrm{N}:\mathrm{H}\\ \times\cdot\\ \mathrm{H}\end{array}\right]^{+}$$

Ammonium chloride or sal-ammoniac, NH_4Cl. It was first prepared by Arabs as a sublimate from the distillation of camel's dung. It can be prepared by neutralising ammonia solution with hydrochloric acid. It is prepared by heating a mixture of sodium chloride and ammonium sulphate ; ammonium chloride formed sublimes and collects as a sublimate.

$$(NH_4)_2SO_4 + 2NaCl = 2NH_4Cl + Na_2SO_4.$$

Ammonium chloride is manufactured by neutralising the ammoniacal liquor of the gasworks with hydrochloric acid and evaporating the resulting solution until crystallisation occurs. The crude product is purified by sublimation.

Ammonium chloride is a white crystalline solid having a sharp saline taste. It is highly soluble in water ; its solution in water is accompanied by the absorption of heat. When heated, its molecule is dissociated into ammonia and hydrogen chloride.

$$NH_4Cl \rightleftharpoons NH_3 + HCl$$

Ammonium sulphate, $(NH_4)_2SO_4$. It is the most important commercial salt of ammonia. The salt is prepared by passing ammonia gas into 60 per cent sulphuric acid and evaporating the resulting solution until crystallisation occurs. It is prepared industrially on a large scale by passing synthetic ammonia into a suspension of gypsum (calcium sulphate) through which carbon dioxide is also passed. A precipitate of calcium carbonate is obtained while ammonium sulphate remains in solution :

$$2NH_3 + CaSO_4 + CO_2 + H_2O = CaCO_3 + (NH_4)_2SO_4$$

It is also manufactured by passing ammonia gas obtained from "ammoniacal liquor" of gasworks or coke-ovens, into sulphuric acid.

Ammonium sulphate is a transparent crystalline solid, isomorphous with potassium sulphate. It is readily soluble in water.

It is used as a reagent in the chemical laboratory and as a source of other ammonium compounds. It is one of the most valuable fertilisers.

Ammonium carbonate or sal volatile, $(NH_4)_2CO_3$. Ammonium carbonate is prepared by subliming a mixture of chalk (calcium carbonate) and ammonium chloride or ammonium sulphate.

$$(NH_4)_2SO_4 + CaCO_3 = (NH_4)_2CO_3 + CaSO_4$$

The sublimate so obtained always contains some bicarbonate, NH_4HCO_3 and carbamate $NH_2.CO.ONH_4$. Ammonium carbamate when dissolved in water is decomposed into ammonium carbonate,

$$NH_2CO.ONH_4 + H_2O = (NH_4)_2CO_3$$

so that solutions of the solid product contain ammonium carbonate.

Ammonium carbonate is used as a reagent in the laboratory and in the manufacture of smelling salt, rubber-accelerators and fire-extinguishing compounds.

Ammonium nitrate, NH_4NO_3. It is prepared by neutralising nitric acid with ammonia :

$$NH_3 + HNO_3 = NH_4NO_3$$

It is also prepared by the double decomposition of ammonium sulphate and calcium nitrate or sodium nitrate in aqueous solution.

$$(NH_4)_2SO_4 + Ca(NO_3)_2 = 2NH_4NO_3 + CaSO_4$$

$$(NH_4)_2SO_4 + 2NaNO_3 = 2NH_4NO_3 + Na_2SO_4$$

The precipitated calcium sulphate is filtered off and ammonium nitrate is crystallised. When sodium nitrate is used, sodium sulphate crystallises out first from the hot solution, and ammonium nitrate separates on cooling.

Ammonium nitrate is a white crystalline solid and readily dissolves in water with the absorption of much heat. It decomposes, when heated, into nitrous oxide and water :

$$NH_4NO_3 = N_2O + 2H_2O$$

Ammonium nitrate when stored in bulk is liable to detonation with disastrous results. High explosives can be prepared by mixing ammonium nitrate with trinitrotoluene (T. N. T.) or picric acid.

Ammonium nitrite, NH_4NO_2. It is prepared by mixing the solutions of equimolecular quantities of sodium nitrite and ammonium chloride and evaporating the resulting solution in vacuum at 60°C.

$$NH_4Cl + NaNO_2 = NH_4NO_2 + NaCl$$

The salt is explosive and deliquescent. It decomposes when heated, into nitrogen and water :

$$NH_4NO_2 = N_2 + 2H_2O$$

Ammonium sulphide $(NH_4)_2S$. When hydrogen sulphide is passed through fairly concentrated ammonia solution, the resulting liquid contains a mixture of ammonium hydrosulphide $(NH_4)HS$ and normal ammonium sulphide $(NH_4)_2S$. Normal ammonium sulphide is also obtained by saturating concentrated ammonia solution with hydrogen sulphide, keeping the solution cold.

$$NH_3 + H_2S = NH_4HS$$
$$NH_3 + NH_4HS = (NH_4)_2S$$

"Yellow ammonium sulphide" is prepared by dissolving flower of sulphur in ammonium sulphide solution ; the resulting solution contains ammonium polysulphide $(NH_4)_2S_x$. Yellow ammonium sulphide solution is used in qualitative analysis.

Ammonium thiocyanate, NH_4SCN. It is prepared by the action of a solution of ammonia in a 50-50 mixture of alcohol and water upon carbon disulphide, CS_2. The thiocarbamate is first formed ; this is decomposed into ammonium thiocyanate when its solution is evaporated :

$$2NH_3 + CS_2 = NH_4SCN + H_2S$$

It is used as a chemical reagent and in dyeing industry to prevent the injurious action of iron salts.

Other salts of ammonia of importance are phosphate, fluoride, bromide, iodide, and oxalate.

OXIDES OF NITROGEN

Nitrogen forms six oxides as shown in table 5.2

Table 5.2

Name	Formula	Oxidation number of nitrogen
Nitrous oxide	N_2O	+1
Nitric oxide	NO	+2
Nitrogen trioxide	N_2O_3	+3
Nitrogen dioxide	NO_2	+4
Nitrogen tetroxide	N_2O_4	+4
Nitrogen pentoxide	N_2O_5	+5

All the oxides of nitrogen are endothermic and, therefore, in principle, are unstable at low temperature. They can all be obtained from nitric acid and its salts. Only the oxides which are included in the syllabus are discussed here.

Nitrous Oxide, N_2O.

The gas was discovered by J. Priestley in 1772 who made it by reducing nitric oxide with moist iron filings :

$$2NO + H_2O + Fe = N_2O + Fe(OH)_2$$

H. Davy, in 1799, prepared the nearly pure gas by heating ammonium nitrate and noticed the physiological effect that gave rise to the name *laughing gas*.

Preparation of nitrous oxide. (i) **From ammonium nitrate. Laboratory method.** In the laboratory, nitrous oxide is prepared by heating ammonium nitrate :

$$NH_4NO_3 = N_2O + 2H_2O$$

Above 250°C, ammonium nitrate decomposes explosively. In order to avoid the risk of explosion, a mixture of sodium nitrate and ammonium sulphate is heated when evolution of nitrous oxide takes place more slowly and uniformly.

$$(NH_4)_2SO_4 + 2NaNO_3 = Na_2SO_4 + 2NH_4NO_3$$

$$2NH_4NO_3 = 2N_2O + 4H_2O$$

$$\overline{(NH_4)_2SO_4 + 2NaNO_3 = Na_2SO_4 + 4H_2O + 2N_2O}$$

A mixture of ammonium sulphate and sodium nitrate is placed in a round bottomed flask fitted with a delivery tube. The flask is heated gently ; nitrous oxide evolved passes through the delivery tube and is collected over hot water, because the gas is perceptibly soluble in cold water.

Purification. Nitrous oxide thus prepared contains nitrogen, nitric oxide, moisture and chlorine. It is purified by passing it successively (a) through a solution of ferrous sulphate to remove nitric oxide ; (b) through caustic soda solution to remove chlorine and (c) through concentrated sulphuric acid to remove moisture. The purified gas is then collected over mercury. The gas still contains a little nitrogen.

(ii) **From nitric acid.** Nitrous oxide may be prepared by treating copper or zinc with dilute nitric acid or by reducing nitric acid with stannous chloride.

$$4Zn + 10HNO_3 = 4Zn(NO_3)_2 + 5H_2O + N_2O$$
$$4SnCl_2 + 2HNO_3 + 8HCl = 4SnCl_4 + 5H_2O + N_2O.$$

(iii) **From hydroxylamine hydrochloride.** Very pure nitrous oxide is obtained by mixing equimolecular solutions of hydroxylamine hydrochloride and sodium nitrite.

$$NH_2OH,HCl + NaNO_2 = NaCl + N_2O + 2H_2O$$

(iv) **By direct synthesis.** Nitrous oxide is formed with difficulty by direct synthesis. It may be formed by passing electric discharge through a mixture of nitrogen and oxygen at low pressure. The reaction is highly endothermic.

$$2N_2 + O_2 = 2N_2O$$

Properties. (A) **Physical properties :** Nitrous oxide is a colourless gas with a faint sweetish odour and taste, and is heavier than air. It dissolves fairly well in cold water without reacting chemically. The solution in water has a sweetish taste. It is more soluble in alcohol.

The gas liquefies at 0°C under a pressure of 30 atms. The liquid boils at $-89{\cdot}5$°C and freezes to a snow-like mass when allowed to evaporate. The solid nitrous oxide melts at $-102{\cdot}4$°C. When breathed for a short time, the gas causes hysteric laughter, this effect led to the use of the name *laughing gas* for the substance. Longer inhalation causes unconsciousness and finally death.

(B) **Chemical properties :** Nitrous oxide decomposes into nitrogen and oxygen at elevated temperatures.

$$2N_2O = 2N_2 + O_2$$

For this reason, a glowing splint when lowered into nitrous oxide bursts into flame much as it does in pure oxygen. Ignited phosphorus, sulphur, charcoal, etc., burn vigorously into nitrous oxide liberating nitrogen :

$$5N_2O + 2P = P_2O_5 + 5N_2 \; ; \; 2N_2O + S = SO_2 + 2N_2$$
$$C + 2N_2O = CO_2 + 2N_2.$$

Metals like sodium, potassium, iron, and magnesium when heated with the gas burn brilliantly, liberating nitrogen :

$$2Na + N_2O = Na_2O + N_2 \; ; \; Cu + N_2O = CuO + N_2$$
$$Mg + N_2O = MgO + N_2.$$

In these reactions, nitrous oxide is first decomposed into nitrogen and oxygen by heat; the burning body then combines with oxygen, leaving nirogen as a residue. If the heat produced is not sufficient to decompose the gas, then it fails to act as a supporter of combustion. Thus, when feebly burning sulphur is introduced into a jar of nitrous oxide, it is extinguished because the temperature is not high enough to decompose the gas.

The following properties serve to distinguish nitrous oxide from oxygen :

Properties	**Nitrous oxide**	**Oxygen**
(1) Smell	Faint sweetish odour	odourless
(2) Density (H=1)	22	16
(3) Solubility in (a) water	Appreciably soluble in cold water. 100 c.c. of water at N.T.P. dissolves 130 c.c. of the gas.	Very slightly soluble in water.
(b) Alcohol	Appreciably soluble in alcohol. 100 c.c. of alcohol at N.T.P. dissolves 418 c.c. of the gas.	Moderately but much less soluble than nitrous oxide.
(4) Treatment with alkaline pyrogallate solution.	The gas is not absorbed.	The gas is readily absorbed.
(5) Treatment with ammoniacal cuprous chloride solution.	No reaction.	The gas is absorbed in the solution giving blue colour.
(6) Treatment with nitric oxide.	No reaction,	Brown fumes are produced due to the formation of NO_2.
(7) White phosphorus is burnt in the two gases contained in two jars;	(i) White phosphorus burns vigorously in the jar.	(i) Phosphorus burns brilliantly.
After combustion the jars are inverted over water.	(ii) Water does not rise into the jar because during burning equal volumes of nitrogen are liberated. $\underset{(5\text{ vols})}{5N_2O}+2P=P_2O_5+\underset{(5\text{ vols})}{5N_2}$	(ii) Water rises up and occupies the whole volume of the jar since oxygen is completely absorbed by phosphorus. $5O_2+4P=2P_2O_5$

Uses. The gas mixed with oxygen or air is used as a general anaesthetic for minor operations.

Nitric Oxide, NO

J. Mayow in 1669 obtained nitric oxide but it was first recognised as a distinct gas by Priestley in 1772. Priestley prepared it by the action of dilute nitric acid on copper or mercury and called it "nitrous air".

Preparation of nitric oxide. Nitric oxide can be prepared by the following processes :

(i) **By the direct combination of nitrogen and oxygen.** Nitric oxide is formed in small quantities from nitrogen and oxygen at very high temperatures.

It is also produced by the action of an electric discharge in air. The oxidation is an endothermic process :

$$N_2+O_2 \rightleftharpoons 2NO-43{\cdot}2 \text{ kcal.}$$

(ii) **From potassium or sodium nitrate.** Pure nitric oxide is prepared by heating a mixture of powdered potassium nitrate, saturated solution of ferrous sulphate and conc. sulphuric acid in a flask. The gas evolved is collected over mercury.

$$6FeSO_4+2KNO_3+4H_2SO_4=3Fe_2(SO_4)_3+2NO+4H_2O+K_2SO_4$$

Nitric oxide can also be prepared by heating a solution of ferrous chloride mixed with hydrochloric acid and sodium nitrate.

$$3FeCl_2+NaNO_3+4HCl=3FeCl_3+NaCl+2H_2O+NO$$

(iii) Pure nitric oxide results when mercury is shaken with potassium nitrate or nitric acid and concentrated sulphuric acid.

$$6Hg+2HNO_3+3H_2SO_4=3Hg_2SO_4+2NO+4H_2O$$

$$6Hg+4H_2SO_4+2KNO_3=3Hg_2SO_4+K_2SO_4+2NO+4H_2O$$

(iv) **From sodium nitrite.** Highly pure nitric oxide can be prepared by dropping a 50 per cent solution of sulphuric acid upon a mixed solution of potassium iodide and sodium nitrite.

$$2KI+2NaNO_2+2H_2SO_4=K_2SO_4+Na_2SO_4+I_2+2H_2O+2NO$$

(v) **From nitric acid. Laboratory preparation.** In the laboratory, nitric oxide is prepared by the action of copper turnings on cold dilute nitric acid :

$$3Cu+8HNO_3=3Cu(NO_3)_2+4H_2O+2NO$$

Copper turnings are taken into a flask fitted with a thistle funnel and a delivery tube (fig. 5.6). A mixture of equal volumes of concentrated nitric acid and water is poured in through the funnel, the reaction at once sets in and the bottle is filled with brown fumes. due to the reactions of nitric oxide with atmospheric oxygen inside the flask :

$$2NO+O_2=2NO_2$$

The brown fumes of NO_2 are readily soluble in water whereas nitric oxide is not ; hence the flask soon clears. Nitric oxide is then collected by the displacement of water in which it is almost insolube.

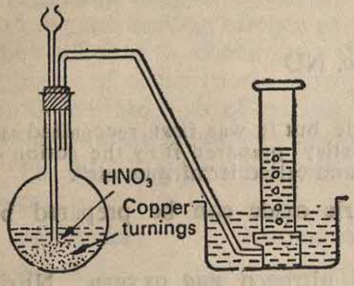


Fig. 5.6

Purification. The gas thus prepared contains nitrogen, nitrous oxide and NO_2. The gas is purified by absorbing it in a strong solution of ferrous sulphate when dark brown compound $FeSO_4{\cdot}NO$ is formed. This dark brown solution, on being heated, evolves nearly pure nitric oxide which is dried by passing the gas through concentrated sulphuric acid. The gas is then collected over mercury.

Properties of nitric oxide. (A) Physical properties : Nitric oxide is a colourless gas and little heavier than air. It is sparingly soluble in water and does not react with it chemically. One volume of water will dissolve only 0·07 volume of NO at 0°C.

The gas is very difficult to condense ; liquefies at –93·5°C under a pressure of 71·2 atmospheres to a colourless liquid. The liquid boils at –150°C and freezes at –160°C to white solid.

It is readily solube in solutions of ferrous sulphate, giving a dark brown liquid containing the unstable compound $FeSO_4.NO$.

(B) **Chemical properties : (i) Stability to heat.** Although the gas is endothermic, it does not decompose unless heated to about 1000°C. It is one of the most stable oxides of nitrogen.

$$2NO=N_2+O_2$$

Hence, the gas is not a ready supporter of combustion. Burning charcoal and sulphur are extinguished when plunged into the gas but vigorously burning phosphorus will continue to burn.

(ii) **Reaction with metals.** Nitric oxide is reduced to nitrogen by strongly heated metals such as sodium, potassium, copper, iron, nickel and magnesium.

$$2NO+4K=2K_2O+N_2\ ;\ 2Cu+2NO=2CuO+N_2$$

$$2Ni+2NO=2NiO+N_2\ ;\ 2NO+2Fe=2FeO+N_2$$

$$2Mg+2NO=2MgO+N_2$$

(iii) Reactions with non-metals. (a) The most characteristic property of nitric oxide is its ability to react with oxygen without being heated, forming brown nitrogen dioxide.

$$2NO+O_2=2NO_2$$

For example, if a cylinder filled with nitric oxide is opened, brown fumes immediately appear at its mouth.

(b) When nitric oxide is sparked with hydrogen, nitrogen is produced.

$$2NO+2H_2=N_2+2H_2O$$

But if a mixture of nitric oxide and hydrogen is passed over a catalyst such as platinum, ammonia is formed.

$$2NO+5H_2=2NH_3+2H_2O$$

Hydroxylamine is formed when nitric oxide is reduced by tin and hodrochloric acid.

$$2NO+6H=2NH_2OH$$

(c) Nitric oxide combines with chlorine in presence of charcoal to form nitrosyl chloride.

$$2NO+Cl_2=2NOCl$$

With bromine it forms nitrosyl bromide and nitrosyl tribromide.

$$2NO+Br_2=2NOBr\ ;\ NOBr+Br_2=NOBr_3$$

Iodine oxidises nitric oxide to nitric acid.

$$2NO+3I_2+4H_2O=2HNO_3+6HI$$

(d) Vigorously burning phosphorus, charcoal, and sulphur will continue to burn in the gas.

$$4P+10NO=2P_2O_5+5N_2$$
$$2NO+C\ \ =N_2+CO_2$$

(iv) **Reaction with compounds.** (a) Nitric oxide reacts slowly with concentrated aqueous potassium hydroxide, forming nitrous oxide.

$$4NO+2KOH=N_2O+2KNO_2+H_2O$$

(b) It is oxidised by powerful oxidising agents such as potassium permanganate.

$$6KMnO_4+10NO+9H_2SO_4$$
$$=10HNO_3+3K_2SO_4+6MnSO_4+4H_2O$$

Sulphurous acid (or sulphur dioxide in presence of water) reduces nitric oxide to nitrous oxide.

$$2NO+H_2SO_3=N_2O+H_2SO_4$$

(c) The gas is readily solube in alkaline solution of sodium sulphite, the solution contains dinitrososulphite.

$$Na_2SO_3+2NO=Na_2(NO)_2SO_3$$

When this solution is acidified, nitrous oxide is evolved.

$$Na_2(NO)_2SO_3 = Na_2SO_4 + N_2O$$

(d) A mixture of nitric oxide and vapours of carbon disulphide produced by shaking a few c.c. of carbon disulphide in a jar of nitric oxide, when kindled, burns with a brilliant blue flame.

$$2CS_2 + 10NO = 2CO + 4SO_2 + 5N_2$$

Tests. (i) It forms brown fumes with oxygen of the atmosphere. (ii) With ferrous sulphate solution it forms an unstable dark brown liquid.

Uses. In the manufacture of sulphuric acid by chamber process, nitric oxide is employed as a carrier of oxygen.

Nitrogen dioxide, NO_2

In 1671, R. Boyle found that nitric oxide formed brown fumes in air. The mentioning of these brown fumes is found in alchemical writings as "the blood of the salamander". Dulong in 1816 prepared liquid nitrogen dioxide, NO_2, by cooling a mixture of nitric oxide and oxygen (2 : 1). Graham called the gas "nitrogen peroxide".

Preparation. (i). From nitric oxide. When a mixture of 2 volumes of nitric oxide and 1 volume of oxygen is passed slowly through a U-tube kept immersed in a freezing mixture, nitrogen dioxide is obtained as a yellow liquid in the U-tube.

$$2NO + O_2 = 2NO_2$$

(ii) **From nitric acid.** Nitrogen dioxide is formed by the action of concentrated nitric acid on copper.

$$Cu + 4HNO_3 = Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

(iii) **From nitrosyl hydrogen sulphate.** When nitrosyl hydrogen sulphate is heated with dry potassium nitrate, nitrogen dioxide is evolved.

$$NO{\cdot}HSO_4 + KNO_3 = 2NO_2 + KHSO_4$$

Nitrosyl hydrogen sulphate is prepared by passing sulphur dioxide slowly into fuming nitric acid in a stoppered retort cooled in a freezing mixture.

$$SO_2 + HNO_3 = NOHSO_4$$

(iv) **From lead nitrate. Laboratory preparation.** In laboratory, nitrogen dioxide is prepared by heating lead nitrate.

$$2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2$$

Dry powdered lead nitrate is heated in a hard glass test tube (fig. 2.4) when a mixture of nitrogen dioxide and oxygen is evolved. The mixed gases are passed through a U-tube cooled in a freezing mixture. Nitrogen dioxide condenses in the U-tube as a pale yellow liquid and oxygen passes out.

Properties. (A) Physical properties : Nitrogen dioxide is a brown gas having a stong and pungent odour and an acid taste. The gas is very poisonous. When cooled, the gas readily condenses to a pale yellow liquid boiling at 22°C. When the liquid is cooled at −10°C, it solidifies to colourless crystals. The solid consists of dinitrogen tetroxide, N_2O_4, which is formed due to the reversible "association" of nitrogen dioxide.

$$\underset{\text{2 vol.}}{2NO_2} \rightleftharpoons \underset{\text{1 vol.}}{N_2O_4} + 12{\cdot}9 \text{ kcal}$$

The association is an exothermic process and hence is favoured by the decrease of temperature. Since there is a decrease in volume the association is also favoured by the increase of pressure. Since N_2O_4 is colourless the gas becomes lighter in colour at low temperatures. At the boiling point, the gas is about 80 per cent N_2O_4 ; at 60°C, NO_2 and N_2O_4 are present in almost equal quantities ; at 140°C the gas consists almost entirely of NO_2. This behaviour is due to the increasing dissociation of N_2O_4 with increasing temperature (fig. 5.7).

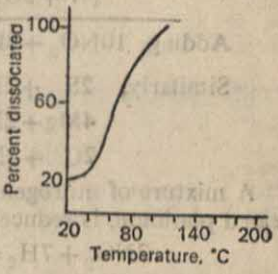


Fig. 5.7

$$N_2O_4 \rightleftharpoons 2NO_2$$

When nitrogen dioxide is heated above 154°C, it begins to dissociate into nitric oxide and oxygen. This dissociation is highly endothermic and is favoured by the increase of temperature. Above 620°C the dissociation is complete (fig. 5.8)

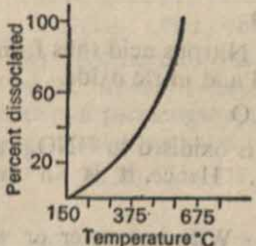


Fig. 5.8

$$2NO_2 \rightleftharpoons 2NO + O_2 - 27{\cdot}1 \text{ kcal.}$$

These changes can be summarised as follows :

$$\underset{\text{(solid)}}{N_2O_4} \overset{-10°C}{\rightleftharpoons} \underset{\text{(liquid)}}{N_2O_4} \overset{22°C}{\rightleftharpoons} \underset{\text{(vapour, 80\%)}}{N_2O_4} \overset{60°C}{\rightleftharpoons} \underset{\text{(in equal amount)}}{(NO_2+N_2O_4)} \overset{140°C}{\rightleftharpoons} 2NO_2 \overset{620°C}{\rightleftharpoons} 2NO+O_2$$

(b) Chemical properties : (i) Reaction with metals. Potassium when heated in nitrogen dioxide, inflames and reduces it to nitric oxide. $K + 2NO_2 = KNO_3 + NO$

Heated metals such as sodium, iron or copper reduce it to nitrogen. $4Cu + 2NO_2 = 4CuO + N_2$

Lead is oxidised by nitrogen dioxide to lead monoxide.

$$Pb + NO_2 = PbO + NO$$

(ii) **Reaction with non-metals.** Nitrogen dioxide is not combustible and does not support combustion. Vigorously burning sulphur, phosphorus or carbon may continue burning in the gas but only when the temperature of combustion is sufficiently high to decompose the gas.

The reason is that at sufficiently high temperature nitrogen dioxide decomposes into nitrogen and oxygen and it is oxygen which burns the elements.

$$(2NO_2 = N_2 + 2O_2) \times 5$$
$$(4P + 5O_2 = 2P_2O_5) \times 2$$

Adding, $10NO_2 + 8P = 5N_2 + 4P_2O_5$

Similarly, $2S + 2NO_2 = 2SO_2 + N_2$

$$4Mg + 2NO_2 = 4MgO + N_2$$
$$2C + 2NO_2 = 2CO_2 + N_2$$

A mixture of nitrogen dioxide and hydrogen when passed over heated platinum, is reduced to ammonia.

$$2NO_2 + 7H_2 = 2NH_3 + 4H_2O$$

(iii) **Reaction with compounds.** (a) Nitrogen dioxide reacts with water, forming a mixture of nitrous acid and nitric acid.

$$2NO_2 + H_2O = HNO_2 + HNO_3$$

Hence, it is called a mixed anhydride. Nitrous acid thus formed is unstable and decomposes into nitric acid and nitric oxide.

$$3HNO_2 = HNO_3 + 2NO + H_2O$$

In this reaction, one molecule of NO_2 is oxidised to HNO_3 and another molecule is reduced to HNO_2. Hence, it is an auto-oxidation-reduction reaction.

Nitrous acid thus obtained is unstable. With hot water or with sufficient quantity of water, it gives a mixture of nitric oxide and nitric acid :

$$(2NO_2 + H_2O = HNO_2 + HNO_3) \times 3.$$
$$3HNO_2 = HNO_3 + 2NO + H_2O$$
$$6NO_2 + 2H_2O = 4HNO_3 + 2NO$$

Or, $3NO_2 + H_2O = 2HNO_3 + NO$

At ordinary temperature and in the presence of excess of air, nitrogen dioxide reacts with water producing nitric acid only.

$$4NO_2 + 2H_2O + O_2 = 4HNO_3$$

(b) It reacts with alkalis forming an equimolecular mixture of nitrate and nitrite.

$$2KOH + 2NO_2 = KNO_3 + KNO_2 + H_2O$$

(c) The gas dissolves in conc. sulphuric acid forming nitrosyl hydrogen sulphate sometimes known as chamber crystals.

$$H_2SO_4+2NO_2=NO.HSO_4+HNO_3$$

(d) Nitrogen dioxide is an energetic oxidising agent. It liberates iodine from potassium iodide and oxidises hydrogen sulphide to sulphur.

$$2KI+NO_2+H_2O=2KOH+NO+I_2$$
$$H_2S+NO_2=H_2O+NO+S$$

It oxidises sulphur dioxide to sulphur trioxide and carbon monoxide to carbon dioxide.

$$NO_2+SO_2=SO_3+NO$$
$$CO+NO_2=CO_2+NO$$

In presence of steam nitrogen dioxide oxidises sulphur dioxide to sulphuric acid.

$$NO_2+SO_2+H_2O=H_2SO_4+NO$$

During oxidation nitrogen dioxide decomposes into nitric oxide and nascent oxygen and it is this nascent oxygen which oxidises different substances. For example,

$$\begin{array}{rcl} NO_2 & = & NO + O \\ SO_2+O & = & SO_3 \\ \hline \text{Adding, } NO_2+SO_2 & = & NO + SO_3 \end{array}$$

(e) Nitrogen dioxide also possesses reducing properties. For example, when it is passed through an acidified solution of potassium permanganate in water it reduces potassium permanganate to manganous salt and is itself oxidised to nitric acid.

$$2KMnO_4+3H_2SO_4+10NO_2+2H_2O$$
$$=K_2SO_4+2MnSO_4+10HNO_3$$

From these reactions it is clear that nitrogen dioxide possesses both oxidising and reducing properties. In nitrogen dioxide, nitrogen is in +4 oxidation state but the highest positive oxidation state in which nitrogen can exist is +5. Hence during the reactions of nitrogen dioxide with powerful oxidising agents, the nitrogen atom can transit from +4 oxidation state to +5 oxidation state by losing electron. Hence, in these reactions, nitrogen dioxide can act as a reducing agent. On the other hand, in the reactions of nitrogen dioxide with strong reducing agents, the nitrogen atom can transit from +4 oxidation state to +3, +2, +1, or −3 oxidation state by gaining electrons. Hence, in these reactions nitrogen dioxide can act as an oxidising agent. In the reaction of nitrogen dioxide with water, nitrogen dioxide is partially oxidised and partially reduced.

$$2\overset{+4}{N}O_2 + H_2O = H\overset{+3}{N}O_2 + H\overset{+5}{N}O_3$$

Hence, it is an example of auto-oxidation reduction reaction.

Oxyacids of Nitrogen

The three oxyacids of nitrogen are shown in table 5.3.

Table 5.3

Name	Formula	Oxidation number of nitrogen	Anhydride
Hyponitrous acid	$H_2N_2O_2$	+1	N_2O
Nitrous acid	HNO_2	+3	N_2O_3
Nitric acid	HNO_3	+5	N_2O_5

Since hyponitrous acid is not included in the syllabus, it is not discussed here.

Nitrous acid, HNO_2

Nitrous acid is an unstable acid which is known only in dilute solution and in the form of salts.

Preparation. (i) The acid is usually prepared by treating cold aqueous solution of sodium or potassium nitrite with dilute sulphuric acid.

$$2NaNO_2 + H_2SO_4 = Na_2SO_4 + 2HNO_2$$

The resulting solution is of pale blue colour. It is a weak acid and can be liberated from its salt even by acetic acid.

$$NaNO_2 + CH_3COOH = HNO_2 + CH_3COONa$$

When nitrogen trioxide is dissolved into water, nitrous acid is formed. $N_2O_3 + H_2O = 2HNO_2$

(ii) An aqueous solution of the acid is best prepared by adding to an aqueous solution of barium nitrite an exact amount of ice-cold dilute sulphuric acid required to precipitate all the Ba^{++} ions in the form of barium sulphate.

$$Ba(NO_2)_2 + H_2SO_4 = BaSO_4 + 2HNO_2$$

Barium sulphate is filtered off—the filtrate is a dilute solution of nitrous acid.

Properties. (i) **Decomposition.** On warming its solution, nitrous acid decomposes rapidly into water and its anhydride, nitrogen trioxide, which in turn decomposes rapidly into nitric oxide and nitrogen dioxide :

$$\begin{array}{l} 2HNO_2 = H_2O + N_2O_3 \\ \underline{N_2O_3 = NO + NO_2} \\ 2HNO_2 = H_2O + NO + NO_2 \end{array}$$

In the cold, the dilute solution of nitrous acid undergoes auto-oxidation-reduction :

$$3H\overset{+3}{N}O_2 = H\overset{+5}{N}O_3 + 2\overset{+2}{N}O + H_2O$$

(ii) **Oxidising and reducing property.** Nitrous acid can act both as an oxidising agent and as a reducing agent. Nitrogen atom contains 5 electrons in its outermost shell. Hence, the highest positive oxidation state in which nitrogen atom can exist in its compounds is +5. Consequently, in its compounds, nitrogen atom can exist in all oxidation states from +5 to −3. The oxidation number of nitrogen in nitrous acid is +3. Hence, in reactions of nitrous acid, nitrogen atom can pass from +3 oxidation state to +4 or +5 oxidation state by losing electrons. Again, nitrogen atom of nitrous acid is also capable of passing from +3 oxidation state to +2, +1, 0 or −3 oxidation state by gaining electrons. Consequently, nitrous acid possesses both oxidising and reducing properties.

(a) **Oxidising property.** Nitrous acid acts as an oxidising agent. Thus it liberates iodine from acidified potassium iodide.

$$2KI + H_2SO_4 = K_2SO_4 + 2HI$$

$$2HI + 2HNO_2 = 2H_2O + I_2 + 2NO$$

It oxidises hydrogen sulphide to sulphur and sulphur dioxide to sulphuric acid.

$$H_2S + 2HNO_2 = 2H_2O + 2NO + S$$

$$SO_2 + 2HNO_2 = H_2SO_4 + 2NO$$

Nitrous acid also oxidises stannous chloride to stannic chloride and ferrous salts to ferric salts.

$$SnCl_2 + 2HCl + 2HNO_2 = SnCl_4 + 2NO + 2H_2O$$

$$2FeSO_4 + H_2SO_4 + 2HNO_2 = Fe_2(SO_4)_3 + 2NO + 2H_2O$$

(iii) **Reducing property.** Nitrous acid also acts as a reducing agent. For example, it reduces permanganate, chromates and bromine water.

$$2KMnO_4 + 3H_2SO_4 + 5HNO_2$$

$$= K_2SO_4 + 2MnSO_4 + 5HNO_3 + 3H_2O$$

$$Br_2 + H_2O + HNO_2 = 2HBr + HNO_3$$

Similarly, nitrous acid reduces chlorine water to hydrochloric acid.

$$Cl_2 + H_2O + HNO_2 = HNO_3 + 2HCl$$

It also reduces hydrogen peroxide.

$$H_2O_2 + HNO_2 = HNO_3 + H_2O$$

(iv) Nitrous acid reacts with ammonium chloride and organic substances containing, $-NH_2$ group such as urea, evolving nitrogen.

$$NH_4Cl + HNO_2 = N_2 + HCl + 2H_2O$$

$$CO(NH_2)_2 + 2HNO_2 = 2N_2 + 3H_2O + CO_2$$

Nitrites. The salts of nitrous acid are called nitrites. Nitrites are more stable and are easily prepared. Almost all the nitrites are soluble ; the only important exception is silver nitrite which is sparingly soluble. The most important of these salts are those of sodium and potassium. Sodium and potassium nitrite may be obtained by heating the corresponding nitrates with finely divided lead.

$$NaNO_3 + Pb = NaNO_2 + PbO$$

The product is extracted with water and lead oxide is removed by filtration. The filtrate is evaporated to crystallisation.

Nitrites are now manufactured by passing an equimolecular mixture of nitric oxide and nitrogen dioxide in the aqueous solution of the appropriate alkali.

$$2KOH + NO + NO_2 = 2KNO_2 + H_2O$$

Sodium nitrite is widely used in the manufacture of dyes of the azo-class.

Tests of nitrite. The nitrites are characterised by the following tests :

(i) Reddish brown fumes are evolved when a nitrite is warmed with dilute sulphuric acid. (ii) A nitrite liberates iodine from acidified potassium iodide, the liberated iodine turns starch solution blue. (iii) Brown colour is formed when a nitrite is treated with meta-phenylene-diamine hydrochloride in hydrochloric acid. (iv) An intense pink colouration is obtained when a nitrite is treated with a mixture of solutions of sulphanilic acid and α-naphthylamine in acetic acid. The tests (iii) and (iv) are very delicate and are utilised for the estimation of nitrites in water.

Nitric acid, HNO_3

Aquafortis (nitric acid) was known to alchemists. Geber (778 A. D.) obtained it by distilling copperas (ferrous sulphate) with saltpetre and alum. In 1650, Glauber made it by distilling a mixture of nitre and sulphuric acid. In 1776, Lavoisier proved that nitric acid contains oxygen. Cavendish in 1784 obtained nitric acid by passing electric discharge through a mixture of nitrogen and moist oxygen.

Free nitric acid formed by lightning occurs in traces in the atmosphere. It is found in nature in the form of its salts of which the most important are nitre (potassium nitrate) and chile saltpetre (sodium nitrate).

Preparation. From potassium nitrate. Laboratory preparation. Nitric acid is a volatile acid. It is prepared in the laboratory by the action of a less volatile acid such as sulphuric acid on sodium nitrate or potassium nitrate. Hydrochloric acid is not used in the preparation of nitric acid since it is volatile. The reaction of sulphuric acid with potassium or sodium nitrate takes place in two stages. At moderate temperature, about 200°C, potassium hydrogen sulphate and nitric acid are formed.

$$KNO_3 + H_2SO_4 = KHSO_4 + HNO_3$$

At higher temperature of about 800°C, a further reaction takes place ; potassium hydrogen sulphate being converted into normal sulphate with the formation of more nitric acid.

$$KNO_3 + KHSO_4 = K_2SO_4 + HNO_3$$

In either stage, nitric acid formed volatilises off and can be readily condensed. However, in laboratory preparation, the reaction is not carried out at higher temperatures because of the following reasons :

(i) Nitric acid partly decomposes into water, oxygen and nitrogen dioxide

$$4HNO_3 = 4NO_2 + 2H_2O + O_2$$

(ii) The glass retort would crack.

(iii) The normal sulphate which is left in the retort in the solid state is very difficult to remove.

Procedure. Equal parts by weight of potassium nitrate and concentrated sulphuric acid are taken in a stoppered glass retort (fig. 5.9). The stem of the retort is introduced into a glass flask which is kept cooled by water. The retort is heated to about 200°C when nitric acid formed volatilises and condenses in the water-cooled flask.

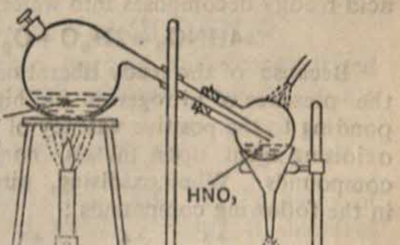


Fig. 5.9

Purification. The acid thus obtained is not pure, and brown in colour. It contains water and oxides of nitrogen. The acid may be concentrated to 98% by redistilling it with twice its weight of concentrated sulphuric acid. The oxides of nitrogen are removed from the acid by blowing dry air through it. Colourless crystals of pure nitric acid are obtained by freezing 98 per cent acid at -42°C.

Properties. (A) Physical properties : Pure nitric acid is a fuming colourless liquid of specific gravity 1·53. It boils at 86°C and freezes at -41°C into a transparent crystalline mass. The pure acid is hygroscopic and rapidly absorbs moisture from air. It has a very corrosive action on the skin and cloth and stains them bright yellow.

It mixes in all proportions with water. A 68% per cent solution which is the usual commercial acid, boils at 120·5 C and can be distilled without alteration. The concentrated nitric acid which contains 96 to 98 per cent HNO_3 is known as the fuming nitric acid. Fuming nitric acid is brown in colour due to nitrogen dioxide dissolved in it.

(B) **Chemical properties :** (i) **Acidic properties.** In aqueous solution the acid is completely ionised into hydrogen ion, H^+ and the nitrate ion, NO_3^-.

$$HNO_3 \rightleftharpoons H^+ + NO_3^-$$

Hence, it is a strong monobasic acid. Its salts are called nitrates. Nitric acid reacts by metathesis with many metallic oxides, hydroxides, carbonates, sulphites and other compounds to yield the nitrates of the metals involved.

$$CaCO_3 + 2HNO_3 = Ca(NO_3)_2 + H_2O + CO_2$$
$$MgO + 2HNO_3 = Mg(NO_3)_2 + H_2O$$
$$NaOH + HNO_3 = NaNO_3 + H_2O$$

(ii) **Instability and oxidising properties.** Nitric acid is not chemically very stable. Upon heating or exposure to light nitric acid readily decomposes into water, oxygen and nitrogen dioxide.

$$4HNO_3 = 2H_2O + O_2 + 4NO_2$$

Because of the ready liberation of oxygen from it and due to the presence of nitrogen in its highest state of oxidation corresponding to the positive valency of 5 nitric acid acts as a powerful oxidising agent upon metals, non-metals and a wide variety of compounds. When oxidising, nitric acid is reduced successively in the following compounds :

$$H\overset{+5}{N}O_3 \rightarrow \overset{+4}{N}O_2 \rightarrow H\overset{+3}{N}O_2 \rightarrow \overset{+2}{N}O \rightarrow \overset{+1}{N}_2O \rightarrow \overset{0}{N}_2 \rightarrow \overset{-3}{N}H_3$$

The degree of reduction of nitric acid depends upon the concentration of HNO_3 and the nature of the reducing agent and its concentration. Concentrated acid is usually reduced to NO_2, dilute acid to NO, and with very dilute acid the chief reduction product is NH_3.

Nitrogen atom contains 5 electrons in its outermost shell. Hence, the highest positive oxidation state of nitrogen atom in its compounds is +5. In nitric acid, the oxidation number of nitrogen is +5 and consequently there is no scope for nitrogen atom in nitric acid to lose electron and to get oxidised. For this reason, nitric acid cannot act as reducing agent ; it acts only as an oxidising agent.

(iii) Reaction with non-metals. Hot concentrated nitric acid oxidises sulphur to sulphuric acid, iodine to iodic acid and phosphorus to phosphoric acid.

$$S+2HNO_3=H_2SO_4+2NO$$

$$3I_2+10HNO_3=6HIO_3+10NO+2H_2O$$

$$3P+5HNO_3+2H_2O=3H_3PO_4+5NO$$

Glowing charcoal burns brilliantly into concentrated nitric acid. When concentrated nitric acid is poured into heated sawdust, the mass often bursts into flame.

$$C+4HNO_3=CO_2+4NO_2+2H_2O$$

(iv) Reaction with compounds. (a) Hot dilute or cold concentrated nitric acid oxidises hydrogen sulphide to sulphur and potassium iodide to iodine.

$$3H_2S+2HNO_3=3S+2NO+4H_2O$$

$$6KI+8HNO_3=3I_2+6KNO_3+2NO+4H_2O$$

Nitric acid oxidises ferrous sulphate in presence of sulphuric acid to ferric sulphate.

$$6FeSO_4+2HNO_3+3H_2SO_4=3Fe_2(SO_4)_3+2NO+4H_2O$$

This reaction occurs quantitatively.

Stannous chloride in hydrochloric acid is oxidised by nitric acid to stannic chloride and nitric acid is reduced to nitrous oxide and ammonia.

$$2HNO_3+4SnCl_2+8HCl=4SnCl_4+5H_2O+N_2O$$

Concentrated nitric acid when warmed with concentrated hydrochloric acid, chlorine, nitrosyl chloride and water are formed.

$$3HCl+HNO_3=Cl_2+NOCl+2H_2O$$

The mixture of conc. HNO_3 and conc. HCl in the ratio of 1 to 3 is known as aqua regia (royal water), because it dissolves noble or royal metals like gold and platinum.

$$Au+4HCl+HNO_3=HAuCl_4^-+NO+2H_2O$$

(b) Nitric acid reacts with many organic substances. In some cases, the oxidation products are formed. In others one or several hydrogen atoms in the molecule of the organic compounds are substituted by nitro group, NO_2. This process known as nitration is of great importance in organic chemistry.

With toluene it gives trinitrotoluene (T.N.T.), with glycerine it gives nitroglycerine and with cellulose it forms nitrocellulose. Both trinitrotoluene and nitroglycerine are violently explosive. Wool or turpentine bursts into flame when they are treated with fuming nitric acid.

(v) **Reaction with metals.** Nitric acid reacts with nearly all of the metals except tantalum, gold, platinum and a few other noble metals. The first product is an oxide which reacts with excess acid to form the corresponding metallic nitrate. Tin, antimony, arsenic, molybdenum and tungsten react with the acid to form the insoluble oxide as the final product. Since the oxidising properties of nitric acid are more pronounced than its acid properties, the reaction of metals with it does not lead to the liberation of hydrogen ; most of the hydrogen which may be liberated are oxidised immediately to water. Only magnesium and manganese liberate hydrogen when they react with very dilute nitric acid (1 or 2 per cent).

$$Mg+2HNO_3=Mg(NO_3)_2+H_2$$

By way of illustrations, the equations of the reactions of nitric acid on some metals are given below.

(a) Reaction of copper with

(i) hot concentrated HNO_3 :

$$Cu+4HNO_3=Cu(NO_3)_2+2H_2O+2NO_2$$

(ii) cold HNO_3 of moderate strength :

$$3Cu+8HNO_3=3Cu(NO_3)_2+4H_2O+2NO$$

(iii) cold and dilute HNO_3 :

$$4Cu+10HNO_3=4Cu(NO_3)_2+5H_2O+N_2O$$

(b) Reaction of zinc with

(i) hot concentrated HNO_3 :

$$Zn+4HNO_3=Zn(NO_3)_2+2H_2O+2NO_2$$

(ii) cold dilute HNO_3 :

$$3Zn+8HNO_3=3Zn(NO_3)_2+4H_2O+2NO$$

(iii) cold very dilute HNO_3 :

$$4Zn+10HNO_3=4Zn(NO_3)_2+3H_2O+NH_4NO_3$$

(c) Reaction of iron with

(i) very concentrated and fuming nitric acid : no reaction ; iron is rendered passive.

(ii) moderately concentrated or hot dilute HNO_3 :

$$Fe+4HNO_3=Fe(NO_3)_3+2H_2O+NO$$

(iii) cold dil. HNO_3 :

$$4Fe+10HNO_3=4Fe(NO_3)_2+3H_2O+NH_4NO_3$$

(d) Reaction of tin with

(i) conc. HNO_3 :

$$Sn+4HNO_3=SnO_2+4NO_2+2H_2O$$

(ii) cold dilute HNO_3 :

$$4Sn+10HNO_3=4Sn(NO_3)_2+3H_2O+NH_4NO_3$$

(e) Reaction of mercury with

(i) hot and concentrated HNO_3.

$$Hg+4HNO_3=Hg(NO_3)_2+2H_2O+2NO_2$$

(ii) cold and dilute HNO_3

$$6Hg+8HNO_3=3Hg_2(NO_3)_2+2NO+4H_2O$$

(f) Reaction of silver with

(i) hot dilute HNO_3 :

$$Ag+2HNO_3=AgNO_3+H_2O+NO_2$$

(g) Cold and dil. HNO_3 reacts with magnesium or manganese to form magnesium or manganese nitrate and hydrogen

$$Mg+2HNO_3=Mg(NO_3)_2+H_2$$

$$Mn+2HNO_3=Mn(NO_3)_2+H_2$$

The reduction products of nitric acid obtained in the reaction of nitric acid with metals can be summarised in table 5.4.

Table 5.4. Dependence of the degree of reduction of HNO_3 with its concentration.

Metals	Concentrated HNO_3	Moderately strong HNO_3 (1 : 1)	Dilute
Copper	NO_2	NO	N_2O
Zinc	NO_2	NO	NH_3
Iron	Passive	NO	NH_3
Tin	NO_2	—	NH_3
Mercury	NO_2	—	NO

The complex nature of the reactions of nitric acid with metals may be explained by assuming that the first product is nascent hydrogen which attacks the excess of nitric acid to give reduction products such as oxides of nitrogen or even ammonia.

$$M+HNO_3=MNO_3+H$$

$$HNO_3+H=H_2O+NO_2$$

$$HNO_3+3H=2H_2O+NO$$

$$HNO_3+8H=3H_2O+NH_3$$

$$2HNO_3+8H=H_2N_2O_2+4H_2O$$

$$H_2N_2O_2=N_2O+H_2O$$

Concentrated nitric acid. Dilute nitric acid on distillation yields 68% nitric acid which distils without change in composition. It has a specific gravity 1·414 and is sold in the market as the concentrated nitric acid.

Fuming nitric acid. When a mixture of concentrated nitric acid and a small quantity of starch or arsenic trioxide is distilled, fuming nitric acid is obtained. It contains dissolved NO_2 and is coloured brown. Fuming nitric acid can also be prepared by passing NO_2 into concentrated nitric acid. It emits fumes continuously and has strong oxidising power.

Aqua regia. A mixture of 1 volume of conc. HNO_3 and 3 volumes of conc. HCl is known as aqua regia. It dissolves noble metals like gold, platinum, etc.

$$Au + 4HCl + HNO_3 = HAuCl_4 + NO + 2H_2O$$

Gold or platinum does not dissolve in conc. HNO_3 or conc. HCl. The nascent chlorine evolved by the reaction of conc. HCl and conc HNO_3 reacts with the metal forming soluble chloride.

$$3HCl + HNO_3 = NOCl + 2Cl + 2H_2O$$

$$2Au + 6Cl + 2HCl = 2HAuCl_4$$

Passivity of metals in concentrated nitric acid. Iron, cobalt and chromium become passive in concentrated nitric acid (sp. gr. 1·5) or fuming nitric acid and lose their chemical activity temporarily. Under this condition, the metals are said to be in the passive state.

A layer of metallic oxide is deposited on the metal as a result of the initial reaction between the metal and conc. HNO_3. This prevents the metal from coming in contact with the acid and consequently the metal becomes passive. If the layer is removed either by rubbing or by reduction with a reducing gas the inactivity of the metal can be removed.

Uses of nitric acid. Nitric acid finds numerous applications both in the laboratory and in industry :

(i) In laboratory, it is used as oxidising agent. It is an important reagent in organic chemistry both for oxidation and nitration.

(ii) It is used in the production of commercial explosive such as trinitrotoluene (T. N. T.) and nitroglycerine and in the manufacture of chemicals, dyes, medicinals and fertilisers.

(iii) It is also used in the production of celluloid, collodion, rayon, lacquers and many modern plastics. Silver nitrate for photographic and other purposes are produced from nitric acid.

(iv) It is also employed for cleaning metals and for etching processes.

Tests of nitric acid and nitrates. Nitric acid and nitrates are detected by the following tests :

(i) When a nitrate is heated with conc. H_2SO_4 and copper turnings, reddish brown fumes are evolved. Brown fumes are evolved when nitric acid is heated with copper turnings alone.

(ii) **Brucine test.** When a solution of brucine in conc. H_2SO_4 is added to a solution of nitrate or nitric acid, red colour is produced.

(iii) **Ring test.** A small quantity of nitrate is dissolved into water in a test tube and an equal volume of concentrated sulphuric acid is added to it. The mixture is cooled. A freshly prepared solution of ferrous sulphate is carefully poured down the side of the test tube into the mixture so that the liquids mix only at the surface of contact. A dark brown ring appearing at the junction of the liquids indicates the presence of a nitrate. Nitrites also respond to the ring test.

Sulphuric acid reacts with the nitrate liberating nitric acid.

$$NaNO_3 + H_2SO_4 = HNO_3 + NaHSO_4$$

Nitric acid is then reduced by ferrous sulphate to nitric oxide.

$$2HNO_3 + 6FeSO_4 + 3H_2SO_4 = 3Fe_2(SO_4)_3 + 2NO + 4H_2O$$

The excess of ferrous sulphate then absorbs nitric oxide yielding brown coloured compound, $FeSO_4.NO$.

$$FeSO_4 + NO = FeSO_4 \cdot NO$$

This compound appears as a brown ring at the junction of the liquids.

Estimation of nitric acid and nitrates. (i) The free nitric acid in absence of other acids can be estimated by titration with standard alkali.

(ii) A nitrate or a nitrite can be estimated quantitatively by the use of Devarda's alloy containing aluminium, copper and zinc. Devarda's alloy yields ammonia quantitatively when heated with a nitrate or nitrite in strongly alkaline solution.

$$NaNO_3 + 4Zn + 7NaOH = NH_3 + 4Na_2ZnO_2 + 2H_2O$$

The ammonia formed is distilled into a measured volume of standard sulphuric acid. The excess of acid is then titrated with standard alkali.

(iii) Nitric acid is reduced quantitatively to nitric oxide by mercury in presence of concentrated sulphuric acid.

$$6Hg + 2HNO_3 + 3H_2SO_4 = 3Hg_2SO_4 + 2NO + 4H_2O$$

A solution containing nitrate is shaken with concentrated sulphuric acid and mercury in Lunge's nitrometer when nitratie is quantitatively reduced to nitric oxide. The volume of nitric oxde is then accurately measured and the weight of the nitrate radical present can be calculated. Nitrites can also be estimated by this method.

Test of nitrate in presence of nitrite. A mixture of nitrate and nitrite is heated with ammonium chloride or urea and sulphuric acid when nitrite decomposes completely into nitrogen. Then the ring test is applied to detect the presence of the nitrate.

The Nitrogen Cycle

Nitrogen is essential to plant and animal life. It is present in plant and animal tissues in compounds known as proteins. But neither most plants nor animals can assimilate the elemental nitrogen of the atmosphere. Only a few leguminous plants such as peas, beans, (including soyabean) and alfalfa can utilise free nitrogen directly. They have on their roots nodules which contain "nitrifying" bacteria which are capable of converting atmospheric nitrogen into compounds which are then assimilated by these plants and are converted into proteins. Most plants can only absorb nitrogen in the form of nitrates. Thus, a supply of nitrogen in the form of nitrates in the soil is essential for the life of the plants. Atmospheric nitrogen is converted into nitrates in the following way: During electrical discharges in the atmosphere, nitrogen unites with oxygen to form nitric oxide. This combines with a further portion of atmospheric oxygen to form nitrogen dioxide which is absorbed by rain water forming nitric acid. Nitric acid is washed down by rains into the soil and is transformed into nitrates by reactions with bases present in the soil.

$$N_2+O_2 \rightleftharpoons 2NO \;;\; 2NO+O_2=2NO_2$$

$$3NO_2+H_2O=2HNO_3+NO$$

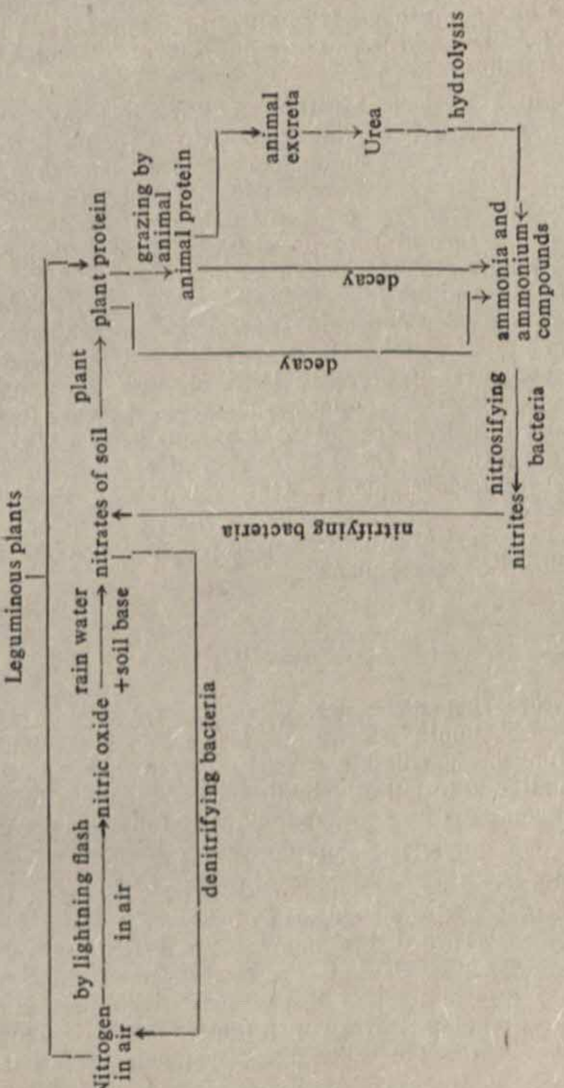
Nitrates from the soil are taken in by plants and are converted by biochemical processes to proteins.

On the other hand, animals acquire their necessary nitrogen by consuming plant proteins as food and convert them into animal proteins. Some animals (carnivorous) obtain their necessary nitrogen by consuming the proteins in other animals. As a result of these processes, nitrogen is continually removed from the air. But it is transferred back to the air by the following processes :

Major part of the nitrogen consumed by animals is returned to the soil in the form of urea in the excreta. Urea is readily hydrolysed forming ammonia and carbon dioxide :

$$CO(NH_2)_2+H_2O=CO_2+2NH_3$$

Again, when bodies of animals and plants decay ammonia is produced. In the soil, this is oxidised by nitrosifying bacteria to nitrites which are oxidised by nitrifying bacteria to nitrates. Nitrates are again assimilated by plants. But there are bacteria in the soil called "denitrifying bacteria" which are capable of abstracting oxygen from the nitrates, liberating free nitrogen. As a result of the activities of the 'denitrifying bacteria" part of the combined



The nitrogen cycle

nitrogen is constantly evolved in the form of free nitrogen which passes to the atmosphere.

Thus, we see that there is a continuous transfer of nitrogen from the air into various systems and back to the air again. The succession of changes through which this transfer occurs is known as nitrogen cycle. The nitrogen cycle in nature is summarised in the above diagram.

Fixation of Nitrogen. Fixation of nitrogen is any process by which atmospheric nitrogen is incorporated into useful nitrogenous compounds. Nitrogen in combination as useful compounds such as ammonia, nitrate, etc., is known as fixed nitrogen. The artificial processes by which nitrogen can be fixed are (i) Haber's process by which ammonia is formed from its elements ; (ii) Birkeland-Eyde process (or arc process) by which nitric oxide is formed from nitrogen and oxygen of the atmosphere and (iii) Cyanamide process by which calcium cyanide is formed from calcium carbide and nitrogen. The formation of nitrides is of some importance. The natural processes by which atmospheric nitrogen is fixed are (i) lightning flashes in the atmosphere—this causes the formation of nitric oxide. This is converted into nitric acid which falls to the earth with rain and (ii) absorption of atmospheric nitrogen by leguminous plants. On the roots of these plants there are nodules which contain nitrifying bacteria. These bacteria convert atmospheric nitrogen into compounds which are assimilated directly by these plants.

APPENDIX

1. To prove that nitric acid contains nitrogen, oxygen and hydrogen. Some pumice stones are taken in a flask fitted with a dropping funnel. The flask is strongly heated and concentrated nitric acid is allowed to fall drop by drop on the pumice stone when nitric acid decomposes in accordance with the following equation :

$$4HNO_3 = 4NO_2 + 2H_2O + O_2$$

The mixture of gases is then allowed to pass through : (i) first U-tube kept immersed in cold water ; steam condenses in this U-tube (ii) second U-tube kept immersed in a freezing mixture ; nitrogen dioxide is condensed here ; the gas coming out is collected in a gas-jar by the displacement of water. This gas rekindles a glowing chip ; gives brown fumes with nitric oxide and is completely absorbed by alkaline pyrogallate. Hence, this gas is oxygen.

To the liquid in the first U-tube, a piece of metallic sodium is added when a gas is evolved. This gas is collected by the displacement of water. It burns in oxygen yielding water and is absorbed by heated palladium. Hence, it is hydrogen.

The liquid in the second U-tube on heating passes in the gaseous state. The gas is then passed through a tube containing copper heated to bright redness when nitrogen dioxide is reduced to nitrogen.

$$4Cu+2NO_2=4CuO+N_2$$

The gas coming out of the tube is collected in a gas-jar by the displacement of water. The gas is absorbed by heated magnesium giving magnesium nitride which on treatment with water forms ammonia. Hence, the gas is nitrogen.

Hence, nitric acid contains hydrogen, oxygen and nitrogen.

(ii) **To prove that lead nitrate contains lead, nitrogen and oxygen.** Some lead nitrate are taken in a hard glass test tube and the tube is then strongly heated Lead nitrate decomposes in accordance with the following equation :

$$2Pb(NO_3)_2=2PbO+4NO_2+O_2$$

Lead oxide remains as solid in the test tube and the mixture of nitrogen dioxide and oxygen is passed through a U-tube kept immersed in a freezing mixture ; nitrogen dioxide condenses in the U-tube and oxygen passes out and is collected. Oxygen is detected by its tests.

Solid left in the tube is heated in a stream of hydrogen when the following reaction takes place.

$$PbO+H_2=Pb+H_2O$$

The residue thus obtained is soft and malleable and marks paper. Hence, it is lead.

The presence of nitrogen is proved by the method described above.

(iii) **To prove that ammonia contains nitrogen and hydrogen.** Ammonia is passed through a tube containing red-hot copper oxide when ammonia is oxidised to nitrogen.

$$2NH_3+3CuO=3H_2O+3Cu+N_2$$

The gas coming out of the tube is collected in a gas-jar by the displacement of water. The gas is absorbed by heated magnesium giving magnesium nitride which on treatment with water forms ammonia. Hence, the gas is nitrogen.

Metallic sodium is placed in a hard-glass tube provided with an inlet tube and a delivery tube. Sodium in the tube is strongly heated and ammonia gas is passed over heated sodium through the inlet tube when the following reaction takes place.

$$2Na+2NH_3=2NaNH_2+H_2$$

The gas coming out of the delivery tube is collected by the displacement of water. This gas burns in oxygen producing water and is absorbed by palladium. Hence, the gas is hydrogen.

Thus it is proved that ammonia contains nitrogen and hydrogen.

(iv) **Distinction between nitrites and nitrates.**

Experiment	Nitrite	Nitrate
(a) To the solution of the salt dilute hydrochloric acid is added.	Evolution of brown fumes.	No brown fumes are evolved.
(b) Dilute solution of potassium permanganate is added to the solution of the salt.	Pink colour of potassium permanganate is discharged.	The colour of the solution is not discharged.
(c) To the solution of the salt is added acetic acid, potassium iodide and starch solution.	Blue colour is developed.	No blue colour is produced.
(d) The sample is boiled with a strong solution of urea or ammonium chloride.	Nitrogen is evolved.	No evolution of nitrogen
(e) A pinch of brucine and a few drops of conc. H_2SO_4 are added to a few c.c. of the solution of the salt.	No red colour.	Deep red colouration slowly changing to yellow.

EXERCISES

1. Describe how you would obtain nitrogen (a) from air, and (b) from ammonia. Describe the laboratory preparation of nitrogen. How would you obtain very pure nitrogen ?

2. How does nitrogen react with magnesium and calcium carbide ? Describe the action of water on the products formed in both cases.

What are the uses of elemental nitrogen ?

3. How would you prepare in the laboratory pure and dry ammonia ? Why is the gas not dried by conc. H_2SO_4, or phosphorus pentoxide ?

How does the gas react with (a) oxygen, (b) sodium, (c) chlorine (d) cupric oxide, (e) ferric chloride solution and (f) copper sulphate solution.

4. How and under what conditions does ammonia react with (a) air, (b) calcium sulphate, (c) mercurous chloride and (d) carbon dioxide ?

5. How may ammonia be converted into (a) nitrogen and (b) nitric acid ? How is ammonia detected ? [C. U., '44]

6. What is ammonium ion ? Give the electronic interpretation of the formation of ammonium ion.

Describe the preparation and uses of some important ammonium salts. How are the ammonium salts detected ?

7. Describe the effect of heat on (a) ammonium nitrite, (b) ammonium chloride (c) lead nitrate (d) nitric acid and (e) ammonium nitrate.

8. How would you prove experimentally that both air and nitrous oxide contain the same constituents ? What is the evidence that in one case the constituents are chemically combined while in the other they merely form a mechanical mixture ? [C. U., '50]

9. Describe the preparation of nitric oxide in the laboratory. What happens when the gas is slowly passed for some time into a jar of air confined over water ? How would you qualitatively distinguish between nitric oxide, nitrous oxide and oxygen ? [C. U. '53]

10. How would you prepare nitric acid in the laboratory ? Describe with equations the reactions of nitric acid with (a) copper, (b) zinc, (c) iron, (d) magnesium, (e) sulphur and (f) iodine.

How would you prove experimentally that nitric acid contains nitrogen, hydrogen and oxygen ?

11. How would you prepare the pure samples of (a) N_2O_4 ; (b) NO ; and (c) N_2O. Why is concentrated nitric acid usually yellow ? How is nitrous oxide distinguished from oxygen ?

12. Starting from nitric acid how would you prepare (a) oxygen, (b) nitrogen, (c) nitrogen dioxide, (d) ammonia and (e) hydrogen. How would you detect nitrate radical ?

13. Describe "nitrogen cycle" in nature. What is meant by the fixation of atmospheric nitrogen ? Discuss briefly the methods used to restore the nitrogen compounds removed from the soil.

14. Describe experiments to show that (a) nitric acid is an oxidising agent and (b) ammonia contains nitrogen and hydrogen.

Describe with equations the action of nitric acid on (a) hydrochloric acid ; (b) ferrous sulphate and phosphorus.

15. Explain the following statements :

(a) Nitrous acid acts both as an oxidising agent and a reducing agent.

(b) NO_2 (brown) becomes lighter in colour when it is cooled.

(c) Feebly burning sulphur is extinguished when introduced in a jar of nitrous oxide but ignited sulphur burns vigorously in nitrous oxide.

(d) Ammonia is basic in character.

(e) Ammonia liberates copper from cupric oxide.

(f) Solution of ammonia in water when neutralised form ammonium salts.

16. How would you prepare (a) nitric acid from ammonia and vice-versa (b) nitrogen from ammonia and vice-versa (c) ammonia from nitric oxide and vice-versa and (d) ammonium chloride from ammonia and vice-versa.

17. A gas (A) is passed over heated magnesium when a compound (B) is formed. The compound (B) on treatment with water gives a gaseous product (C) which when passed over heated cupric oxide the original gas (A) is formed. When the gas (C) is passed over heated sodium, a gas (D) is formed. The gases (A) and (D) react to give the gas (C). Identify (A), (B), (C) and (D). [Ans. (A) $\rightarrow N_2$; (B) $\rightarrow Mg_3N_2$; (C) $\rightarrow NH_3$ (D) $\rightarrow H_2$]

18. A compound (A) on heating with an excess of caustic soda solution liberates a gas (B) which gives white fumes on exposure to HCl. Heating is continued to expel the gas completely. The resultant alkaline solution again liberates the same gas (B) when heated with zinc powder. However,

the compound (A) when heated alone does not give nitrogen. Identify (A) and (B). [Ans. A → NH_4NO_3 ; B → NH_3] [I. I. T., '73]

19. Starting with gaseous nitrogen, oxygen and hydrogen, indicate giving balanced equations, how would you prepare the following compounds: HNO_3 and N_2O. [I. I. T., '67]

20. A solid substance (A) is boiled with aqueous solution of sodium hydroxide when a gas (B) is evolved and a salt (C) is formed. Gas (B) on treatment with potassium mercuric iodide, K_2HgI_4 gives an orange yellow precipitate. The alkaline solution left after the complete removal of the gas (B) on boiling with zinc dust gives the same gas (B). Identify (A), (B) and (C). [Ans. A → NH_4NO_3, B → NH_3 and C → $NaNO_3$]

21. When a sodium salt (A) was strongly heated, oxygen and a solid (B) was formed. When treated with dilute hydrochloric acid (B) gave a brown gas. When (B) was heated with NH_4Cl a colourless gas was evolved and a solid residue (C) was formed. (A) on heating with NH_4Cl liberated a colourless gas and a residue same as (C) was formed. Identify (A), (B) and (C) and give equations for each reaction. [Ans. (A) → $NaNO_3$; (B) → $NaNO_2$; (C) → NaCl.]

22. State what happens when :

(i) nitrogen is passed over heated magnesium and the product which is formed is treated with water.

(ii) nitrogen is passed over heated calcium carbide and the product obtained is treated with water.

(iii) a mixture of air and ammonia is passed over heated platinum catalyst.

(iv) ammonium hydroxide is gradually added to copper sulphate solution. [H. S., '78]

(v) sodium nitrate is heated with conc. H_2SO_4.

(vi) a copper coin is dipped into conc. HNO_3.

(vii) a solution of sodium nitrate is heated with zinc dust and sodium hydroxide and the gas which is evolved is passed into sulphuric acid.

(viii) glowing charcoal is dipped into concentrated nitric acid.

(ix) sulphuretted hydrogen is passed into cold concentrated nitric acid.

(x) ferrous sulphate solution is added to a cold dilute solution of sodium nitrate acidified with concentrated sulphuric acid.

(xi) a mixture of ammonium chloride and slaked lime is heated and the gas obtained is passed over heated cupric oxide.

(xii) a mixture of nitric oxide and hydrogen is passed over heated spongy platinum.

(xiii) nitric oxide is passed through a solution of potassium permanganate acidified with sulphuric acid.

(xiv) nitrogen dioxide is passed through an alkali solution.

(xv) ammonia gas is passed over molten sodium. [H. S., '78]

(xvi) ammonium nitrate is heated. [H. S., '78]

(xvii) ammonium dichromate is heated.

(xviii) a mixture of ammonia and carbon dioxide is heated to a high temperature.

(xix) a mixture of ammonium chloride and sodium nitrite is heated.

(xx) sodium nitrate solution is heated with potassium hydroxide and aluminium.

(xxi) nitric oxide gas is passed into ferrous sulphate solution acidified with sulphuric acid. [H. S., '78]

23. (a) Why is the nitrogen obtained from air heavier than that obtained from NH_4NO_3 ? [H. S., '79]

(b) Prove that nitric acid contains oxygen.

(c) Why does nitric oxide become brown when exposed to air ?

CHAPTER VI

BORON AND ITS COMPOUNDS

Atomic weight, 10·811 Atomic number, 5

Electronic configuration, $1s^2\ 2s^2\ 2p^1$

Boric acid was first prepared by Homberg in 1702 by subliming borax with green vitriol ($FeSO_4, 7H_2O$). Davy in 1807 first obtained boron as an olive-brown powder by electrolysing moist boric acid. Gay-Lussac and Thenard prepared boron in 1808 by the reduction of boron trioxide with potassium.

Free boron does not occur in nature. Boron occurs as boric acid and as salts of various polyboric acids. The principal boron minerals are *borax*, ($Na_2B_4O_7 . 10H_2O$); *kernite* ($Na_2B_4O_7, 4H_2O$); *colemanite* ($Ca_2B_6O_{11}, 5H_2O$); *boronatrocalcite* ($CaB_4O_7, NaBO_2, 8H_2O$); and *boracite* ($2Mg_3B_8O_{15}, MgCl_2$). A major portion of the world's supply of boron compounds is produced by the United States. Free boric acid, H_3BO_3 is found in the hot springs or "fumaroles" of Tuscany in Italy.

Preparation. Boron exists in two forms; amorphous and crystalline. Amorphous boron can be prepared by the following methods.

(i) Amorphous boron is obtained when boron trioxide is heated with sodium, potassium, magnesium or aluminium in a covered crucible. A violent reaction takes place :

$$B_2O_3+3Mg=2B+3MgO$$

The fused mass is cooled and boiled with dilute hydrochloric acid when magnesium oxide dissolves in hydrochloric acid leaving boron as an amorphous brown powder. Brown powder of boron is then filtered, washed and dried. Amorphous boron thus obtained is not pure. Excess of magnesium must be avoided because it combines with the freed element to form a boride.

(ii) Amorphous boron can also be obtained by the action of potassium or magnesium on potassium borofluoride.

$$3K+KBF_4=4KF+B$$

(iii) Pure crystalline boron is obtained by subjecting a mixture of hydrogen and boron trichloride to the action of the electric arc struck between water-cooled copper electrodes.

$$2BCl_3+3H_2=2B+6HCl$$

Boron so prepared is a black very hard infusible solid with a conchoidal fracture. Its properties are quite different from those of amorphous variety. Crystalline boron can also be obtained by fusing the amorphous boron and then cooling.

99% pure boron can be prepared by the electrolysis of a fused mixture of potassium fluoborate, KBF_4, the oxide B_2O_3 and KCl at about 1000°C.

Properties. (A) Physical properties. Amorphous boron is a brownish powder while crystalline boron is said to be colourless and to resemble diamond in both brilliance and hardness. But the crystalline boron is usually obtained as a lustrous black solid which is contaminated with metallic borides. Amorphous boron has a specific gravity of 1·73 ; and its melting point is 2,300°C while crystalline form has a specific gravity of 2·3. Both varieties of the element are poor conductors of electricity but their conductivity increases as the temperature is raised.

(B) Chemical properties. (i) Boron possesses principally the properties of a non-metal. At room temperature, it does not react with oxygen but it burns in oxygen at 700°C or in air at 1500°C with a green flame. The reaction is highly exothermic.

$$4B+3O_2=2B_2O_3$$

(ii) Boron ignites spontaneously in fluorine forming boron trifluoride. $2B+3F_2=2BF_3$

It reacts with chlorine and bromine in an analogous way but higher temperatures are required to initiate the reactions. The tri-iodide is not formed by the direct combination of the elements.

(iii) Boron combines directly with nitrogen forming boron nitride. Boron nitride is formed when boron is heated in an atmosphere of nitrogen, ammonia, nitric oxide or air.

$$2B+N_2=2BN\ ;\ 5B+3NO=3BN+B_2O_3$$

Boron nitride is readily hydrolysed by steam.

$$BN+3H.OH=NH_3+H_3BO_3$$

(iv) Boron unites with carbon at very high temperatures forming boron carbide. It also reacts with sulphur upon being heated forming boron trisulphide, B_2S_3.

$$4B+C=B_4C$$

Boron carbide is among the hardest substances known and is used as an abrasive.

(v) At elevated temperatures, boron combines with most metals forming metallic borides.

$$3Mg+2B=Mg_3B_2$$

(vi) Boron is oxidised by concentrated sulphuric acid and nitric acid to orthoboric acid.

$$B+3HNO_3=H_3BO_3+3NO_2$$

Aqueous solution of hydrogen peroxide and other oxidising agents also oxidise boron to orthoboric acid.

(vii) Boron dissolves in fused alkalis liberating hydrogen and forming borates.

$$2B+6NaOH=2Na_3BO_3+3H_2$$

(viii) Boron plays an important part in the life of plants. For the normal growth of many agricultural crops such as cotton, tobacco, sugar beet, etc., small quantities of boron compounds in the soil are necessary.

Boron compounds. Boron is positively trivalent in its compounds except in the case of the hydrides in which it shows anomalous valencies.

Boric acid (more accurately orthoboric acid). Boric acid has the formula H_3BO_3. It is also known as boracic acid. The acid occurs naturally in the hot springs of Italy's volcanic region.

Preparation. Boric acid is prepared by adding concentrated hydrochloric acid to a hot saturated solution of borax ; colourless soapy crystals of boric acid separate when the solution is cooled.

$$Na_2B_4O_7+2HCl+5H_2O=2NaCl+4H_3BO_3$$

The crystals are washed with hot water and are then purified by recrystallisation from hot water.

Boric acid is prepared commercially from the naturally occurring deposits of calcium borates called *colemanite.* The mineral is powdered and suspended in boiling water ; sulphur dioxide is then passed into the suspension when boric acid and calcium bisulphite are formed. On cooling, boric acid crystallises out.

$$Ca_2B_6O_{11}+2SO_2+9H_2O=2CaSO_3+6H_3BO_3$$
$$2CaSO_3+2SO_2+2H_2O=2Ca(HSO_3)_2$$

Properties. (A) Physical properties. Boric acid or orthoboric acid is a white crystalline substance which is greasy to the touch. It is sparingly soluble in cold water but fairly soluble in hot water. If a solution of boric acid is boiled, some of boric acid will come away together with water vapour. This accounts for its presence in volcanic gases.

(B) Chemical properties. (i) When orthoboric acid is heated to 100°C ; it loses water to form metaboric acid which above 140°C further loses water to give tetraboric acid. On heating to a still higher temperatures, it is converted into a glassy mass of boron trioxide.

$$H_3BO_3 \overset{100^\circ C}{=} HBO_2+H_2O$$
$$4HBO_2 \overset{140^\circ C}{=} H_2B_4O_7+H_2O$$
$$H_2B_4O_7=2B_2O_3+H_2O$$

(ii) Boric acid is a very weak acid and its salts are, therefore, hydrolysed by water. It ionises as : $H_3BO_3 \rightleftharpoons H^+ + BO_2^- + H_2O$ and hence acts as a monobasic acid.

It reacts with alkalis according to the equation.

$$H_3BO_3 + NaOH = NaBO_2 + 2H_2O$$

Boric acid can be titrated with sodium hydroxide in presence of excess of glycerol using phenolphthalein as an indicator. Glycerol increases the strength of boric acid.

Uses. Boric acid is used as an antiseptic in medicine. It can be safely used as an antiseptic eye wash. It is also used in the manufacture of glasses, enamels and certain paints. It was once used as a food preservative but its use for this purpose is now forbidden in many countries.

Borax $Na_2B_4O_7$, $10H_2O$. Borax is the sodium salt of tetraboric acid (i.e., sodium tetraborate). It occurs naturally as *tincal* in the dried up inland lakes of some parts of India, Tibet and California. About 55% of borax is present in native tincal from which borax is obtained by treating the mass with hot water, filtering and cooling the filtrate when crystals of borax separate out.

Manufacture of borax. (a) From colemanite. Colemanite is first finely powdered and then boiled with aqueous solution of sodium carbonate. Calcium carbonate is precipitated and a mixture of borax and sodium metaborate is formed :

$$Ca_2B_6O_{11} + 2Na_2CO_3 = 2CaCO_3 + Na_2B_4O_7 + 2NaBO_2$$

The precipitates of calcium carbonate are filtered off and the clear filtrate is then allowed to crystallise when crystals of borax separate. The mother liquor contains sodium metaborate which is converted into borax by blowing carbon dioxide through it. Second crop of crystals of borax are obtained by crystallising the solution.

$$4NaBO_2 + CO_2 = Na_2B_4O_7 + Na_2CO_3$$

(b) From boric acid. It is also manufactured by neutralising with sodium carbonate the boric acid obtained from boracite.

$$4H_3BO_3 + Na_2CO_3 = Na_2B_4O_7 + 6H_2O + CO_2$$

The solution thus obtained on crystallisation yields crystals of borax.

Properties. Borax forms large, colourless crystals which effloresce in dry air. It is soluble in water ; the solution is alkaline because borax undergoes hydrolysis forming sodium hydroxide and boric acid.

$$Na_2B_4O_7 + 7H_2O \rightleftharpoons 2NaOH + 4H_3BO_3$$

Since methyl orange is not affected by boric acid, the solutions of borax can be titrated with standard hydrochloric acid using methyl orange as an indicator.

When heated borax loses its water of crystallisation and swells to form a porous opaque mass which upon further heating melts into a transparent vitreous mass, called borax bead. Borax bead dissolves the oxides of various metals forming metallic metaborates when heated with them, and from the colours of the borax beads the metals in the salts can be identified. The colour of the bead also depends on the nature of the flame of Bunsen burner, i.e., whether it is oxidising or reducing.

$$\mathrm{Na_2B_4O_7{,}10H_2O} = \mathrm{Na_2B_4O_7+10H_2O}$$

$$\mathrm{Na_2B_4O_7} = \mathrm{2NaBO_2+B_2O_3}$$

$$\left.\begin{aligned} \mathrm{CuO+B_2O_3} &= \underset{\text{(copper metaborate)}}{\mathrm{Cu(BO_2)_2}} \\ \mathrm{CuO+NaBO_2} &= \mathrm{NaCuBO_3} \end{aligned}\right\}\text{ oxidising flame}$$

$$\left.\begin{aligned} \mathrm{2Cu(BO_2)_2+C} &= \underset{\text{(cuprous metaborate)}}{\mathrm{Cu_2(BO_2)_2}}\mathrm{+CO+B_2O_3} \\ \mathrm{Cu_2(BO_2)_2+C} &= \underset{\text{(red)}}{\mathrm{2Cu}}\mathrm{+CO+B_2O_3} \end{aligned}\right\}\text{ reducing flame}$$

$$\mathrm{CoO+B_2O_3} = \underset{\text{(cobaltous metaborate)}}{\mathrm{Co(BO_2)_2}}$$

$$\left.\mathrm{Fe_2O_3+3B_2O_3} = \underset{\text{(ferric metaborate)}}{\mathrm{2Fe(BO_2)_3}}\right\}\text{ oxidising flame}$$

$$\left.\mathrm{2Fe(BO_2)_3+C} = \underset{\text{(ferrous metaborate)}}{\mathrm{2Fe(BO_2)_2}}\mathrm{+B_2O_3+CO}\right\}\text{ reducing flame}$$

Characteristic bead colours of certain metals are given below :

Table 6.1

Compounds of	Colour of borax bead in	
	Oxidising flame	Reducing flame
Copper	Blue	Red (opaque)
Chromium	Green	Green
Cobalt	Blue	Blue
Manganese	Amethyst	Colourless
Iron	Yellow	Bottle green
Nickel	Reddish brown	Gray (opaque)

Uses. Borax is used (i) in the manufacture of glass, enamels and glazes ; (ii) in medicine and in making medicinal soap (iii) as flux to remove metallic oxide scales from metal surfaces on which welding or soldering is to be done (iv) as a laboratory reagent to test analytically the presence of metals whose glassy metaborates have characteristic colours (v) in the manufacture of drying oils and varnishes for metals (vi) for stiffening candle-wicks and (vii) for glazing paper and playing cards.

Tests of boric acid and borates. (i) When borates are warmed with the methanol CH_3OH in presence of concentrated sulphuric acid, there is evolved volatile methyl borate which on ignited burns with a green flame.

$$2Na_3BO_3+3H_2SO_4=3Na_2SO_4+2H_3BO_3$$

$$H_3BO_3+3CH_3OH=(CH_3)_3BO_3+3H_2O$$

In the case of free boric acid, sulphuric acid need not be added.

(ii) A strip of turmeric paper when moistened with concentrated aqueous solution of borate acidified with hydrochloric acid, is turned brown.

EXERCISES

1. What is borax ? How is it obtained on a commercial scale ? What are the uses of borax ? [C. U. '28, '44]

2. Starting from borax, how would you obtain (a) boric acid and (b) boron. [C. U., '44]

3. Write equations for the following : (a) hydrolysis of $Na_2B_4O_7$ (b) hydrolysis of BF_3 (c) hydrolysis of boron nitride and (d) hydrolysis of calcium boride.

4. Describe a method for the preparation of boric acid. Write equations to show the reaction of boron with : (a) bromine, (b) oxygen (c) sulphur and (d) fluorine.

5. What is the borax bead test ? How is it made and for what types of substances is it of value ? Describe the chemistry of borax bead test.

6. What happens when

(a) orthoboric acid is heated.
(b) boric acid is added to sodium hydroxide solution.
(c) boron tri-oxide is heated with magnesium.
(d) nitrogen is passed over heated boron and the resulting compound is allowed to react with steam.
(e) a mixture of cupric oxide and borax is heated in oxidising flame.
(f) a mixture of sodium borate, conc. sulphuric acid and methyl alcohol is heated.
(g) a mixture of cupric oxide and borax is heated in reducing flame.
(h) carbon di-oxide is passed through an aqueous solution of metaborate.

7. Explain the following statements :

(a) aqueous solution of borax is alkaline.
(b) aqueous solution of borax can be titrated with hydrochloric acid using methyl orange as an indicator.
(c) boric acid, H_3BO_3 is a mono-basic acid.
(d) boric acid can be titrated with sodium hydroxide in the presence of glycerine using phenolphthalein as an indicator.

CHAPTER VII

CARBON AND ITS COMPOUNDS

Atomic weight, 12·011 Atomic number, 6

Electronic configuration, $1s^2\ 2s^2\ 2p^2$

Carbon occurs in nature both as free element and in the combined state. Elementary carbon is found as diamond and as graphite. It is found as carbon dioxide in the air (0·03%). Carbon is found combined with hydrogen in natural gas and petroleum as hydrocarbon. In combination with oxygen, it occurs very abundantly in carbonates such as limestone, marble and chalk, $CaCO_3$ and magnesite, $MgCO_3$. All living matter, both plant and animal, is composed of substances the main constituent of which is carbon. The products of the decay of plant and animal (e.g., coal, oil, etc.) also contain carbon. Various kinds of mineral coal form huge deposits at many points of the globe. Some mineral coal contains as much as 99 per cent carbon Thus, carbon is one of the most abundant elements on the earth although it constitutes only 0·032% of earth's crust. About one million or more than ninetenths of all known compounds contain carbon. Because of vast number and diversity of carbon containing compounds, special branch of chemistry known as organic chemistry is devoted solely to their study.

Allotropic forms of carbon. The elemental carbon exists in three allotropic modifications, e.g., diamond, graphite and amorphous carbon. Diamond and graphite are crystalline in structure. The third form, amorphous carbon, exists in many varieties such as coal, charcoal, coke, etc., of which some have been shown to be microcrystalline form of graphite.

(i) **Diamond. Occurrence.** Diamond occurs naturally in south Africa, Brazil, Ural mountains, India, Borneo and Australlia. The chief source of diamond is South Africa where diamonds are present in a curious type of rock called *blue-ground*. These rocks are present in pipes called diamond-pipes which are thought to be the neck of extinct volcanoes. It occurs usually in the form of small crystals embedded in rocks or disseminated through placer deposits. Large diamond-deposits occur in Congo and South Africa. Indian diamond occurs in alluvial deposit and river gravels.

The largest diamond ever found was the *Cullinan diamond* found in South Africa in 1905. It weighed 3106 carats (1 carat = 0·20 gram). The *Pitt or regent diamond* weighed 136¼ carats. The weight of world famous *Kohinoor diamond* was 106 carats. The *Hope diamond* (44¼ carats) has an exquisite blue colour.

The exact origin of naturally occurring diamond is not known but it is very probable that they were formed at vast depths under great pressure and were crystallised out from a lava or magma which consists largely of magnesium silicate.

Properties. Diamond forms transparent crystals which are colourless when pure. They are usually tinted a faint yellow but may be coloured red, blue or green due to slight impurities. Some diamonds are dark grey and even black ; they exhibit a more or less imperfect crystalline structure and are known as imperfect or black diamonds (also known as boart or carbonado). Black diamonds have no value as gems but are used in tools for cutting and drilling and for polishing other stones.

The density of diamond is 3·5 gram/ml and its refractive index (2·4) is abnormally high. The brilliance of a diamond is due to its high refractive index ; when white light passes through a diamond, it is broken up into its primary colours. Diamond is the hardest substance known. Because of its hardness and high refractive index, it is especially valued as a gemstone. Diamond is a non-conductor of electricity ; it melts above 3500°C.

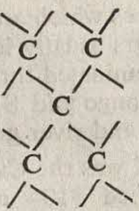
Chemically, diamond is very inert and resists the action of most chemical reagents. When heated in air or oxygen at high temperatures, it burns forming carbon dioxide. If diamond is heated in the absence of air, it turns slowly into graphite.

$$\text{C (diamond)} \rightarrow \text{C (graphite)}$$

It is not attacked by acids ; it is slowly oxidised to carbon dioxide by hot solution of potassium dichromate in concentrated sulphuric acid. It also reacts with sulphur at 1000°C and with fused sodium carbonate.

Diamond is transparent to X-rays whereas the imitation diamond which is made of glass is opaque to the rays.

Structure of diamond. In the diamond crystal, each carbon atom is surrounded by four other carbon atoms at the corner of a regular tetrahedron. A diagram of the tetrahedral arrangement of the carbon atoms is shown in the following figure.



Each carbon atom is joined by a single covalent bond with each of four other carbon atoms. Each of these four carbon atoms is bonded to three others in addition to the original one. The structure is continuous so that the whole crystal is truly a "giant molecule". Many of the covalent bonds are to be broken in order to break the crystal. This requires a vast amount of energy and hence diamond is the hardest known substance. The melting point of diamond is higher than that of any other substance. Because its electrons are tightly held in covalent bonds and are not free to move, diamond is a non-conductor of electricity.

Artificial diamond. Many attempts were made to prepare artificial diamonds by compressing carbon at high temperatures. But until recently, these attempts were fruitless. Only in 1955, American and Swedish scientists succeeded in producing synthetic diamonds by using very high pressures (around 70 to 100 thousand atmospheres) and prolonged heating at about 3000°C. The procedures were based on precise theoretical calculations. The diamonds obtained in the form of yellow crystals were no bigger than grains, but their genuineness has been established by X-ray analysis.

Uses of Diamond. Diamond is generally used as a gemstone. It is used industrially for cutting glass and drilling rocks. Black diamonds have no value as gem. They are used in tools for cutting and drilling and for polishing other stones. Diamond is cut by other diamonds. Finely cut and perfectly transparent diamonds are called *brilliants.*

(b) **Graphite.** Graphite (Greek ; meaning "write") is widely distributed in nature. Large deposits occur in Ceylon, India, Siberia, United States, Canada, Bavaria, Bohemia and elsewhere. It occurs also in the form of fine crystals in many meteorites.

Properties. Graphite is a soft, grey-black, crystalline substance which is greasy to the touch ; it has a lustre somewhat resembling that of a metal. Its specific gravity varies from 2·17 to 2·3. It is a good conductor of heat and electricity. Graphite leaves a black mark when drawn across the paper. This is basis of the use of graphite for the manufacture of lead pencil. At one time, it was thought that graphite contains lead and it was, therefore, called black lead or plumbago.

Graphite is slightly more chemically reactive than diamond. It burns readily in oxygen forming carbon dioxide, but it does not undergo any change when heated in the absence of air or oxygen. Chromic acid oxidises it to carbon dioxide. Pure graphite is not attacked by dilute acids, chlorine and fused alkaline hydroxides. It is slowly oxidised to carbon monoxide by fused sodium carbonate. It reacts with fluorine at 500°C forming carbon tetrafluoride CF_4. Below 100°C, graphite is oxidised slowly by a mixture of nitric acid, sulphuric acid and potassium chlorate to a yellow insoluble solid known as *graphitic acid* which breaks down into *mellitic acid*, $C_6(COOH)_6$. Diamonds are not attacked by the mixture and ordinary charcoal is converted into a brown mass soluble in water.

Artificial graphite. Synthetic graphite is made by *Acheson process* as follows : A mixture of anthracite coal or coke, pitch and sand is placed between the electrodes of a rectangular fire-brick furnace. The electrodes are made up of graphite. Carbon rods are used as core between the terminals. A powerful current is passed through the mixture. The mixture between the electrodes becomes very hot due to its great resistance and in about 24 to 36 hours the carbon is converted into graphite. Silicon carbides are first formed but at high temperatures of the furnace (about 3500°C) these decompose yielding graphite and the silicon volatilises :

$$SiO_2+3C=SiC+2CO \; ; \; SiC=Si+C \text{ (graphite)}$$

Structure of graphite. Graphite crystallises in hexagonal plates. The structure of graphite crystal is shown in fig. 7.1. The carbon atoms are located at the corners of regular hexagons which are arranged in parallel planes. The double bonds are not in fixed positions so that resonance forms are possible. The forces bonding the carbon atoms within a hexagon are very strong. The distance between the adjacent carbon atoms of the hexagon (1·42Å) is less than that between the adjacent planes of hexagon (3·4Å)· Hence the carbon atoms in different planes are attracted to each other by weaker forces. Because of the weakness of these forces (interplanar forces), graphite is very soft and flaky. Out of four valence electrons of each carbon atom, only three electrons are involved in the formation of covalent bonds with three neighbouring carbon atoms. The fourth electron becomes delocalised and is free to move from one layer to other. Consequently, graphite is a good conductor of electricity.

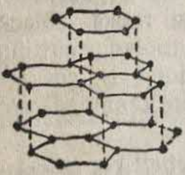


Fig. 7.1

Uses of graphite. (i) Since graphite is a good conductor of electric current, it is used in the manufacture of electrodes, (ii) It is used in the production of lead pencils, the higher the proportion of graphite in the pencil, the softer is the "lead". (iii) It is used in fillers for drycells, and as a lubricant. Because of its resistance to oxidation, graphite is used in making crucibles for use at high temperatures. (iv) It is used for battery plates and electric-light carbons. (v) Graphite in colloidal suspension in water or in oil is used as a lubricant under the commercial names of *Aquadag* and *Oildag*.

Amorphous carbon. When carboniferous compounds are heated in the absence of air, carbon is formed in the form of a black mass called amorphous carbon. The principal varieties of amorphous carbon are : charcoal, coke, coal and lampblack.

(a) Charcoal. The main varieties of charcoal are described below :

(i) Wood charcoal. This is prepared by the destructive distillation of wood. Air-dried woods are placed in large iron retorts from which air is excluded. The retorts are heated externally to a very high temperature. The volatile matter driven off is led through a condenser in which a watery condensate called the pyroligneous acid is separated. From pyroligneous acid, acetic acid, wood alcohol (methyl alcohol) and acetone can be extracted. The solid residue of wood charcoal which amounts to about one-fourth of the mass of original wood is left in the retort.

Wood charcoal is a black amorphous material which is highly porous. It absorbs many times its volume of gases such as NH_3, H_2S, Cl_2, etc. For this property, charcoal is used as an adsorbent for toxic gases in the canister of gasmask. The adsorptive power of charcoal is greatly increased by heating it at 850°C to 900°C in a stream of air or steam. This increases the surface area of charcoal by breaking down the pores and removing any initially adsorbed gases. Charcoal obtained after such treatment is known as *activated charcoal.*

A very active form of charcoal is made by heating cocoanut shell in absence of air.

(ii) **Sugar charcoal.** This is the purest amorphous carbon. It is made by heating pure cane sugar in absence of air :

$$C_{12}H_{22}O_{11}=12C+11H_2O$$

The resulting charcoal is boiled with acids in order to free it from mineral matter. It is then ignited in a current of chlorine to remove the last traces of hydrogen. It is next washed with distilled water and dried by heating in a current of pure and dry hydrogen till no more hydrogen chloride is evolved.

(iii) **Animal charcoal (or bone charcoal or bone-black).** Bone charcoal is obtained as the residue from the destructive distillation of degreased bones in closed retorts. The volatile products consisting of ammonia, pyridine and other substances distil off.

The distillate from bones is known as *bone oil* or *Dippel's oil* and is a source of quinoline and other organic chemicals. The residue in the retort contains about 10 per cent of carbon disseminated through a porous mass of about 80 per cent calcium and magnesium phosphate. The product obtained by removing calcium and magnesium phosphates and other salts by digesting the residue with hydrochloric acid is known as *ivory black.*

Blood charcoal is prepared by charring blood by the similar treatment.

Bone charcoal has very high adsorptive capacity especially with respect to organic dyes. It is used to remove various kinds of colouring matter from solutions. Animal charcoal is used for decolourising sugar syrup. The decolourising power of charcoal can be demonstrated by boiling some indigo solution with powdered animal charcoal and filtering. The filtrate is a colourless liquid. The colouring matter is adsorbed on charcoal and retained by it. The charcoal left after decolourising substances can be revived by boiling it with caustic soda solution and washing. Bone black is revived on being heated to redness in closed retort.

Properties of charcoal. (a) **Physical properties :** Charcoal is a black porous substance ; its specific gravity is 1·3 to 1·9. On account of its porosity, charcoal possesses large surface area and it possesses the property of retaining various substances on its surface. This property is called adsorption. The gases which are adsorbed on charcoal are evolved again on heating. But when charcoal is cooled in liquid air, it adsorbs almost all gases except hydrogen, neon and helium and produces an almost perfect vacuum. It floats on water owing to the fact that it contains adsorbed air. If air is removed by placing the charcoal in water in a bottle connected with air pump, the charcoal gives out bubbles and sink.

Charcoal is not soluble in water, alkalis and in non-oxidising acids. Amorphous carbon melts at about 3500°C.

(b) **Chemical properties :** Charcoal is chemically the most reactive form of carbon, probably due to its large surface area. It ignites in oxygen above 400°C forming carbon dioxide.

$$C+O_2=CO_2$$

Under ordinary conditions, charcoal does not combine with hydrogen and at elevated temperatures and high pressures, it combines with hydrogen forming methane in small quantities. It readily combines with fluorine forming carbon tetrafluoride.

$$C+2F_2=CF_4$$

Chlorine, bromine and iodine do not react with charcoal. At high temperatures, it combines with sulphur forming carbon disulphide ; the reaction is endothermic.

$$C+2S=CS_2$$

Charcoal combines with a few metals such as lithium, calcium and aluminium at high temperatures forming metal carbides ; some metals such as strontium and barium form carbides when their oxides are heated with carbon. At elevated temperatures, charcoal combines with silicon forming silicon carbide or carborundum, SiC.

Concentrated sulphuric acid oxidises charcoal to carbon dioxide.

$$C+2H_2SO_4=CO_2+2SO_2+2H_2O$$

Charcoal is also oxidised to carbon dioxide by hot concentrated nitric acid.

$$C+4HNO_3=CO_2+2H_2O+4NO_2$$

At high temperatures, charcoal acts as a good reducing agent. It reduces the oxides of many metals such as copper, lead, iron and zinc to the respective metals. Thus, when a mixture of charcoal and litharge (PbO) is heated in a crucible, either carbon monoxide or carbon dioxide is evolved and lead remains behind.

$$PbO+C=Pb+CO\ ;\ 2PbO+C=2Pb+CO_2$$

Similarly, cupric oxide is reduced to metallic copper.

$$CuO + C = Cu + CO$$

Lamp black. Lamp black or carbon black is made by burning natural gas and other substances rich in carbon (turpentine, petroleum, tar, etc.) in a limited supply of air and passing the smoke into large chambers in which the coarse "blankets" are suspended. The small particles of carbon collect on the blankets as flaky deposits known as "soot". This is subsequently removed. The 'soot" is one of the purest varieties of carbon, containing 98·6% 'carbon and 1·4% hydrogen. It is a bad conductor of heat and electricity.

Lamp black is used in printers' and India ink, shoe polish and black paint. It is also employed as a filler in the manufacture of rubber tyres.

Coal. Coal is a complex carbonaceous material of vegetable origin. It was formed during an early geological age (about 250 million years ago) when earth was covered with dense foliage. The layers of this vegetation were buried due to the upheavals of the earth's crust as a result of earthquakes and other telluric processes and were thus subjected to high temperatures and pressures. A slow decomposition of the vegetation then took place underground in the absence or in a limited supply of air. As a result, hydrogen and oxygen were eliminated and the residue become increasingly rich in carbon. Thus, the vegetation was first converted into peat, then into lignite (brown coal), then into bituminous (soft coal) and finally into anthracite (hard coal). The carbon content is highest in the anthracite and lowest in the 'peat'.

Peat. It is the product of the first stage of formation of coals. It has a relatively low carbon content which does not exceed 65 per cent and has low fuel value due to its high ash content.

Peat coke is made by the dry distillation of peat. Peat coke contains very little sulphur and hence is suitable for smelting high quality iron.

Lignite or brown coal. It is more compact than peat and is lustrous and brown in colour. It contains 65 to 70 per cent carbon. Brown coal has high ash content and hence a low fuel value.

Bituminous coal. It is the commonest variety and contains 75 to 90 per cent carbon. It is the most widely used of all mineral coals. Bituminous coal is black, hard and brittle. It burns with a smoky flame because of the evolution of large amount of volatile material. *Cannel coal* is a compact non-lustrous variety which is dull-grey or black in colour. Splinters of cannel coal ignite so readily that they burn like a candle. It gives large amount of gas and little coke and is almost exclusively used for gas-making.

Anthracite or Hard Coal. Anthracite is the oldest of the mineral coal. It is very hard, dense, black and brittle and shows no trace of vegetable origin in its structure. It contains about 95 per cent carbon. It contains very little volatile matter and hence burns with practically no smoke and flame. Anthracite coal burns slowly and gives an intense heat. It is used chiefly as a fuel.

Coke. Coke is prepared by heating bituminous coal to 900 – 1200°C in the absence of air. This process is known as destructive distillation of coal because many decomposition reactions occur and the volatile products are distilled off. The residue consisting mainly of carbon is called coke.

Coke is now manufactured in a by-product coke oven which is a brick chamber surrounded by heating flues and furnished with a pipe. The oven is loaded with bituminous coal and heated in absence of air to about 1100°C for a period of 12 to 14 hours. The volatile substances are thus vaporised and the vapours are passed through the pipe to the by-product plant where they are separated. When the coking period is over, one of the sides of the oven is removed and the coke left in the oven is pushed out by a large ram. The white-hot coke is then sent to a quenching tower where it is sprayed with cold water. One ton of bituminous coal yields 1400 pounds of coke.

Large quantities of coke are used for the manufacture of various gaseous fuels. It is largely used for the reduction of oxide ores of metals, particularly iron and in the preparation of quicklime, phosphorus, carbon disulphide and other substances.

Oxides of Carbon

Carbon forms two common oxides, e.g., carbon monoxide, CO and carbon dioxide, CO_2. Both of them are gases at ordinary temperatures.

Carbon monoxide CO.

Carbon monoxide was made by Lassone in 1776 by heating zinc oxide with charcoal. Cruickshank in 1800 proved that it was an oxide of carbon containing less oxygen than carbon dioxide. Clement and Desormes determined the composition of the gas more accurately in 1802.

Carbon monoxide rarely occurs free in nature. Minute traces are found in volcanic gases and in meteorites. Tobacco smoke and the gases from blast and other furnaces contain carbon monoxide. It is an important constituent of fuel gases such as water gas, producer gas and coal gas.

Preparation. Carbon monoxide can be prepared by several methods :

(i) **By the combustion of carbon in a limited supply of oxygen.** When a slow current of oxygen is passed through a tube full of red-hot coke, carbon monoxide is formed.

$$2C + O_2 = 2CO$$

At 500°C, carbon burns even in a limited supply of oxygen yielding almost pure carbon dioxide. But above 1000°C, the product of such a reaction with excess carbon is almost pure carbon monoxide.

When air is passed through red-hot coke, a combustible mixture of carbon monoxide and nitrogen is formed. This mixture (30—40% CO) called producer gas is used as industrial fuel.

(ii) **By the reduction of carbon dioxide with carbon.** Carbon dioxide can be reduced to carbon monoxide by passing it over red-hot coke or charcoal contained in a tube :

$$CO_2+C=2CO$$

Below 400°C, practically no reduction takes place while above 1000°C the reduction is almost complete. Any carbon dioxide which escapes reduction is removed from carbon monoxide by passing through potassium hydroxide solution in which carbon dioxide is absorbed. Carbon monoxide is then collected over water or mercury.

(iii) **By the reaction of red-hot coal or coke with steam.** If a current of steam is blown through a bed of red-hot coke or coal, the two react producing hydrogen and carbon monoxide.

$$C+H_2O=CO+H_2$$

The resulting mixture has a very high fuel value and is known as water gas.

(iv) Carbon monoxide is obtained as a by-product when the more refractory oxides such as those of zinc, iron or manganese are reduced with charcoal or coke.

$$ZnO+C=Zn+CO$$

It is also formed when calcium carbonate or barium carbonate is strongly heated with charcoal.

$$CaCO_3+C=CaO+2CO$$

(v) **By dehydration of oxalic acid or formic acid. Laboratory preparation.** In the laboratory, carbon monoxide is prepared best by heating either formic acid or oxalic acid with a dehydrating agent such as concentrated sulphuric acid. Sulphuric acid abstracts the elements of water from formic acid or oxalic acid liberating carbon monoxide.

$$HCOOH+[H_2SO_4]=CO+[H_2O+H_2SO_4]$$
$$H_2C_2O_4+[H_2SO_4]=CO+CO_2+[H_2O+H_2SO_4]$$

In the case of oxalic acid, carbon dioxide is also formed and must be removed by passing the gas through a solution of alkali.

A suitable quantity of concentrated sulphuric acid (say 100 c. c.) is taken in a flask fitted with a dropping funnel and a delivery tube. The flask is heated gently and formic acid is added drop by drop from the dropping funnel onto the sulphuric acid. Carbon monoxide evolved is passed through a wash bottle containing concentrated solution of caustic potash to remove traces of carbon dioxide and sulphur dioxide which are formed by the reduction of sulphuric acid.

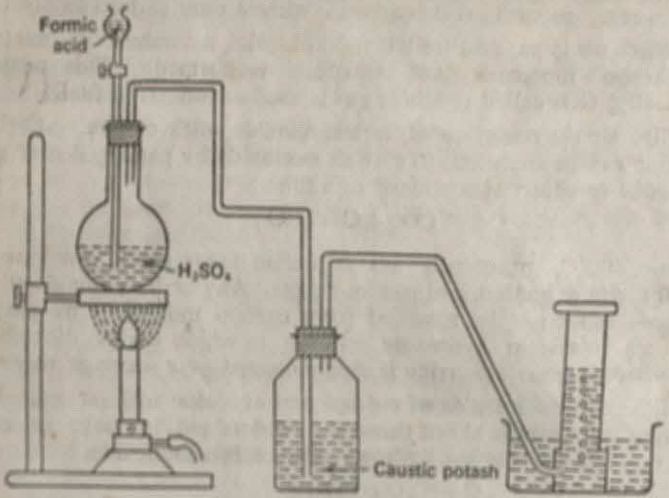


Fig. 7.2

$$H_2SO_4+CO=H_2O+SO_2+CO_2.$$

The gas is then collected over water or mercury. It can be dried by means of phosphorus pentoxide or calcium chloride before being collected over mercury. The gas thus obtained is very pure.

When crystals of oxalic acid is warmed with concentrated sulphuric acid in a flask, a mixture of equal volumes of carbon dioxide and carbon monoxide is evolved. The gas mixture is then passed successively through two wash bottles containing concentrated solution of potassium hydroxide to remove carbon dioxide completely. Carbon monoxide is then collected over water.

Properties. (A) Physical properties : Carbon monoxide is a colourless, tasteless and nearly odourless gas. The gas condenses to a colourless transparent liquid at −192°C and solidifies at −207°C. It is very slightly soluble in water and does not react with water chemically. It is freely soluble in the solution of cuprous chloride in hydrochloric acid or in ammonia. Carbon monoxide resembles nitrogen in many of its physical properties. Both the gases have the same molecular weight (28). Boiling point and solubility of carbon monoxide correspond closely with those of nitrogen.

The gas is extremely poisonous; one volume of carbon monoxide in 800 volumes of air is fatal when breathed for half an hour. When inhaled the gas combines with haemoglobin of the blood to form a relatively stable compound carboxy-haemoglobin which is not decomposed by oxygen. Haemoglobin which has reacted with carbon monoxide is thus unable to perform its normal function of oxygen carrier. Death occurs when about one-third of haemoglobin in the blood has been converted into carboxy-haemoglobin. The poison is insidious since it has no colour, no taste and no odour. The "after damp" in coal mines owes its poisonous character to carbon monoxide formed during an explosion of fire-damp or coal dust. Canaries are very susceptible to carbon monoxide poisoning and the miners in rescue operations generally take down them in cages to give warning of its presence. Recently, instrumental techniques have been devised to determine the concentration of carbon monoxide. Carbon monoxide can be absorbed by respirators containing a mixture of metallic oxides (MnO_2, CuO, Co_2O_3, Ag_2O) called *hopcalite* which serves as a catalyser, causing it to be oxidised to carbon dioxide.

(B) **Chemical properties**: At ordinary temperatures, carbon monoxide is not very active chemically but when heated or in presence of a suitable catalyst it shows a high degree of chemical activity. In carbon monoxide, the oxidation state of carbon is $+2$ and hence it reacts to form more stable $+4$ state.

(i) Carbon monoxide is a stable gas and is not decomposed at high temperatures. It burns in air or oxygen with a bluish flame to form carbon dioxide.

$$2CO+O_2=2CO_2+136 \text{ kcal.}$$

Since a large amount of heat is liberated during this reaction carbon monoxide is largely used in mixture with other gases as a gaseous fuel. A mixture of air or oxygen with carbon monoxide is highly explosive but the explosion does not take place easily if the mixture is absolutely dry.

(ii) Carbon monoxide unites directly with chlorine in sunlight or in presence of a charcoal catalyst to form carbonyl chloride or phosgene.

$$CO+Cl_2=COCl_2$$

Phosgene is a poisonous gas and was used during world war I as chemical warfare agent.

Similarly, carbonyl sulphide is formed when a mixture of carbon monoxide and sulphur vapour is passed through a hot tube.

$$CO+S=COS$$

(iii) Methane and carbon dioxide are formed by passing a mixture of carbon monoxide and hydrogen over nickel catalyst at 380°C.

$$2CO + 2H_2 = CH_4 + CO_2$$

In the prsence of zinc oxide with some chromium oxide at 350°C and under the influence of high pressure, carbon monoxide unites with hydrogen to form methyl alcohol (wood alcohol).

$$CO + 2H_2 = CH_3OH$$

Methyl alcohol is manufactured in large quantities by this reaction.

(iv) Carbon monoxide unites directly with certain metals at elevated temperatures and under pressure to form compounds known as metal carbonyls.

$$Fe + 5CO = Fe(CO)_5 \; ; \; Ni + 4CO \rightleftharpoons Ni(CO)_4$$

Metal carbonyls are highly volatile liquid or solid which are insoluble in water but soluble in many organic solvents. They decompose on heating into corresponding metal and carbon monoxide.

(v) Carbon monoxide is a neutral oxide and does not react with water to form formic acid. But under a pressure of several atmospheres and at a temperature of 200°C it reacts with alkalis to form its salts, formates. Thus sodium hydroxide reacts with carbon monoxide to form sodium formate.

$$NaOH + CO = HCOONa$$

(vi) **Reducing property.** In CO, the oxidation state of carbon is +2. Carbon usually exists in +2 and +4 state ; the +4 state being more stable than +2 state. In reactions of CO, therefore, carbon transits from +2 oxidation state to +4 oxidation state. Consequently, CO is a very good reducing agent. Oxides of iron, lead, copper, etc., are reduced by carbon monoxide to the corresponding metals.

$$CuO + CO = Cu + CO_2 \; ; \; PbO + CO = Pb + CO_2$$

It reduces iodine pentoxide to iodine :

$$I_2O_5 + 5CO = I_2 + 5CO_2$$

Water is reduced to hydrogen when a mixture of steam and carbon monoxide is passed over a catalyst usually Fe_2O_3 heated to 500°C.

$$H_2O + CO \rightleftharpoons H_2 + CO_2$$

Tests. (i) Carbon monoxide burns with a blue flame forming carbon dioxide which turns lime water milky.

(ii) A piece of white filter paper moistened with a solution of palladous chloride when exposed to carbon monoxide is turned pink, green or black due to the reduction of palladous chloride by carbon monoxide to palladium :

$$PdCl_2 + H_2O + CO = Pd + 2HCl + CO_2$$

(iii) A small quantities of carbon monoxide in air can be detected by shaking diluted blood with the air, adding ammonium sulphide solution to it and examining the resulting solution spectroscopically. The presence of two absorption bands is the evidence of the presence of carbon monoxide.

The solution obtained after shaking diluted blood with the air on treating with a solution of tannin gives a red precipitate if carbon monoxide is present while normal blood gives brown precipitate.

(iv) Iodine pentoxide is readily reduced by carbon monoxide to iodine at 90°C :

$$5CO + I_2O_5 = I_2 + 5CO_2$$

The liberated iodine may be titrated with standard thiosulphate solution and the quantity of carbon monoxide is calculated from the data thus obtained. The liberated iodine gives a violet solution with chloroform or carbon disulphide. This is a very sensitive test of the gas.

Uses of carbon monoxide. (i) Carbon monoxide is used as a fuel either in the form of producer gas or water gas. (ii) It is used as a reducing agent in the extraction of metals. Carbon monoxide is employed in the extraction of nickel from its ores where its use depends upon the formation and subsequent decomposition of nickel carbonyl. (iii) It is used in the manufacture of methanol (wood alcohol). It is employed in the manufacture of gasoline by Fischer-Tropsch process. (iv) Carbon monoxide is used for the manufacture of phosgene which is used in the dye industry and in chemical warfare. (v) It is also used in the synthesis of sodium formate.

Structure of carbon monoxide. The structure of carbon monoxide molecule is best represented as a resonance hydrid of the following possible structures :

$$:C\equiv O: \qquad :C=\ddot{O}: \qquad :C-\underset{\cdot\cdot}{\ddot{O}}:$$

Carbon dioxide, CO_2

Carbon dioxide was first discovered in about 1630 by J. B. Van Helmont who prepared it by the action of acids on calcareous substances. J. Black in 1755 called the gas "fixed air". In 1783, Lavoisier showed that it was an oxide of carbon and called it the "carbonic acid gas". The composition of the gas was first determined by Lavoisier.

Carbon dioxide occurs in the atmosphere in the free state to the extent of about 0·03% by volume. Large quantities of carbon dioxide pass into the atmosphere by the combustion of carbonaceous fuels, respiration of animals, decay of organic matter and decompositions of carbonates. It is found in certain mineral waters. Since carbon dioxide is heavier than air, it is inclined to collect as a gas in old deep wells, in depressions in ground near lime kilns and in certain localities such as the Poison valley in Java and Grotta del Cane near Naples where carbon dioxide is evolved through vents and fissures in the earth's crust. Certain depressions in the neighbourhood of extinct volcanoes such as that near the Rhine are constantly filled with carbon dioxide. Animals entering such places are suffocated and die.

In combination, it occurs as carbonates of calcium such as lime-stone, marbles, chalk, etc., and of magnesium such as dolomite and magnesite.

Preparation of carbon dioxide. (i) By the combustion of carbon or compounds of carbon in air or oxygen. On heating in excess of air or oxygen, amorphous carbon reacts vigorously with oxygen forming carbon dioxide.

$$C+O_2=CO_2$$

Methane and ethyl alcohol also burn in excess of oxygen yielding carbon dioxide :

$$CH_4+2O_2=CO_2+2H_2O$$

$$C_2H_5OH+3O_2=2CO_2+3H_2O$$

All such combustions are exothermic

(ii) By the thermal decomposition of metal carbonates and hydrogen carbonates. Large quantities of carbon dioxide are produced by heating calcium carbonate (limestone) at a red heat :

$$CaCO_3=CaO+CO_2$$

Pure carbon dioxide is evolved when pure sodium bicarbonate is heated :

$$2NaHCO_3=CO_2+Na_2CO_3+H_2O$$

(iii) By the fermentation of sugar (glucose). Large quantities of carbon dioxide are produced by the fermentation of sugars or substances containing sugars by the catalytic action of enzymes present in yeast.

$$C_6H_{12}O_6=2C_2H_5OH+2CO_2$$

Alcohol is the principal product and carbon dioxide is the by-product.

(iv) By the action of acids on carbonates. Laboratory preparation. In the laboratory, carbon dioxide is usually prepared by the action of dilute hydrochloric acid on marble, limestone or chalk (calcium carbonate) :

$$CaCO_3+2HCl=CaCl_2+H_2O+CO_2$$

Dilute sulphuric acid is not used in the preparation because calcium sulphate formed is very sparingly soluble and forms a coating on lumps of limestone or marble.

$$CaCO_3+H_2SO_4=CaSO_4+CO_2+H_2O$$

This coating of calcium sulphate prevents marble or limestone from coming in contact with the acid and consequently further reaction is stopped.

Some small pieces of marble are placed in a Woulfe's bottle and covered with water. The Woulfe's bottle is fitted with a thistle funnel and a delivery tube. Moderately strong hydrochloric acid is then added through the thistle funnel the end of which dips into the liquid. Rapid effervescence takes place and carbon dioxide is evolved. The gas is collected by the upward displacement of air.

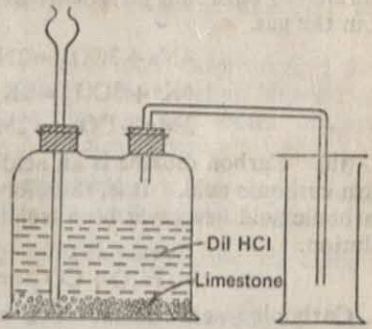


Fig. 7.3

Purification. The gas thus obtained contains HCl vapour. It is passed through sodium bicarbonate solution to remove hydrogen chloride and then through concentrated sulphuric acid to remove moisture. The gas is finally collected over mercury.

Properties. (A) **Physical properties :** Carbon dioxide is a colourless, odourless gas with slightly sour taste. It is heavier than air and dissolves fairly readily in water. At a pressure of 60 atm and at the ordinary temperatures, carbon dioxide condenses to a colourless liquid. The liquid freezes at $-56{\cdot}6$°C under a pressure of 5·2 atmospheres to a snow-white solid which sublimes at -78°C under normal pressure. Because of its high vapour pressure and consequent ability to sublime, solid carbon dioxide is known as *dry ice.*

(B) **Chemical properties :** (i) Carbon dioxide is very stable with respect to heat ; at 2000°C it is only 1·8% dissociated into carbon monoxide and oxygen :

$$2CO_2 \rightleftharpoons 2CO + O_2$$

At high temperatures, therefore, carbon dioxide may act as an oxidising agent.

(ii) **Oxidising properties.** Carbon usually exists in $+2$ and $+4$ oxidation state in its compounds. In carbon dioxide, carbon exists in its highest oxidation state, viz., $+4$. So in reactions of carbon dioxide, carbon is only capable of going from $+4$ state to any other lower oxidation state. Hence carbon dioxide is only capable of acting as oxidising agent. Carbon dioxide is reduced by red-hot carbon, iron or zinc to carbon monoxide :

$$CO_2 + C = 2CO$$
$$CO_2 + Fe = CO + FeO$$
$$CO_2 + Zn = CO + ZnO$$

Certain very active metals whose affinity for oxygen is considerably greater than that of carbon reduce carbon dioxide to carbon at high temperatures. Thus, ignited sodium, potassium and magnesium continue to burn in a jar of carbon dioxide, withdrawing the oxygen from the gas.

$$4Na + 3CO_2 = 2Na_2CO_3 + C$$
$$4K + 3CO_2 = 2K_2CO_3 + C$$
$$2Mg + CO_2 = 2MgO + C$$

(iii) Carbon dioxide is an acidic oxide ; it dissolves in water to form carbonic acid. It is, therefore, known as carbonic anhydride. Carbonic acid has never been isolated and is known only in aqueous solution.

$$H_2O + CO_2 \rightleftharpoons H_2CO_3$$

Carbonic acid forms two series of salts, namely, normal carbonate, e.g., Na_2CO_3 and the hydrogen carbonates or bicarbonates, e.g., $NaHCO_3$. If carbon dioxide is passed through a solution of sodium hydroxide, normal sodium carbonate is first formed :

$$2NaOH + CO_2 = Na_2CO_3 + H_2O$$

but if excess of the gas is passed through the solution, sodium bicarbonate results :

$$NaOH + CO_2 = NaHCO_3$$

If carbon dioxide is passed into lime water, calcium carbonate is precipitated and the lime water is turned milky :

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$$

However, if carbon dioxide is passed through lime water for a long time, the liquid is first turned milky, then gradually begins to be clear and finally becomes quite transparent. The precipitate dissolves owing to the formation of the soluble bicarbonate :

$$CaCO_3 + H_2O + CO_2 = Ca(HCO_3)_2$$

The milkiness appears on boiling the solution or if the solution is left standing for a long time in the air, since the bicarbonate decomposes liberating carbon dioxide and forming calcium carbonate back.

$$Ca(HCO_3)_2 = CaCO_3 + CO_2 + H_2O$$

Carbon dioxide unites with oxides of active metals to form the corresponding carbonates :

$$CaO + CO_2 = CaCO_3$$
$$Na_2O + CO_2 = Na_2CO_3$$

(iv) Since carbon dioxide is formed by the complete oxidation of carbon, it neither burns nor supports combustion. It is, therefore, used as a fire-extinguisher. As little as 2·5% carbon dioxide in air will extinguish a burning candle.

Carbon dioxide is not poisonous to higher animals but it does not support respiration and animals die in it from suffocation. About 5% of the gas mixed with oxygen serves as a stimulant to respiration.

(v) In the presence of ultraviolet light and chlorophyll (the green colouring matter of plants), plants convert carbon dioxide of the atmosphere, and water into sugars, starches and other organic compounds. The process is known as photosynthesis.

Tests. (i) Carbon dioxide extinguishes a burning candle. (ii) Lime water is turned milky when the gas is passed through it.

Uses of carbon dioxide. (i) The most important use of carbon dioxide is in the growth of plants.

(ii) It is used in the production of carbonated beverages. The solubility of carbon dioxide in water is increased by pressure. "Lemonade" and "soda water" are aqueous solution of carbon dioxide under a pressure of 3 to 4 atmospheres.

(iii) Carbon dioxide is employed in industry in various ways. It is used in the manufacture of sodium carbonate by Solvay's process, in the refining of sugar and in the manufacture of salicylic acid and urea. It is used in the manufacture of pigment known as white lead, a basic lead carbonate.

(iv) Since carbon dioxide is a non-supporter of combustion, it is used as a fire-extinguisher. There are several types of carbon dioxide fire-extinguisher.

A diagram of a common type of fire-extinguisher is shown in fig. 7.4. It consists of a strong metal cylinder, which is almost completely filled with a concentrated solution of $NaHCO_3$. At the top of the cylinder, there is a glass bottle containing conc. sulphuric acid. To set the fire-extinguisher off, it is inverted and the glass bottle is broken by a plunger mounted at the cap. The two liquids mix and a violent reaction takes place liberating a large amount of carbon dioxide :

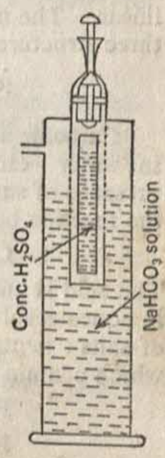


Fig. 7 4

$$NaHCO_3 + H_2SO_4 = NaHSO_4 + H_2O + CO_2.$$

The pressure set up by the accumulating gas forces the mixture of liquid and gas through a nozzle with sufficient force over the flame.

Another type of fire-extinguisher built on the same general principle as above contains sulphuric acid and a solution containing baking soda ($NaHCO_3$) and aluminium sulphate. Aluminium sulphate reacts with baking soda to form a suspension of aluminium hydroxide :

$$Al_2(SO_4)_3+6NaHCO_3=2Al(OH)_3+3Na_2SO_4+6CO_2$$

Sulphuric acid reacts with sodium bicarbonate forming carbon dioxide and the pressure set up by the gas throws a stream of a foamy suspension of aluminium hydroxide which is highly effective in blanketing oil fires. The froth is stabilised with a small amount of licorice or similar organic material.

Another type of fire-extinguisher consists of a cylinder filled with liquid carbon dioxide under pressure. When the valve of the cylinder is opened, a stream of gaseous carbon dioxide is emitted through a funnel shaped nozzle. The chief advantage of this type of fire-extinguisher is that it leaves no liquid residue which might damage any substances not affected by fire.

(v) Carbon dioxide is used as a stimulant to respiration.

(vi) Solid carbon dioxide is used as a refrigerant and in the packing of frozen foods and in various types of coolers.

Structure of carbon dioxide. The carbon dioxide molecule is linear. The molecule is best represented as a resonance hybrid of three structures :

$$:\ddot{O}=C=\ddot{O}: \qquad :O\equiv C-\underset{\cdot\cdot}{\ddot{O}}: \qquad :\underset{\cdot\cdot}{\ddot{O}}-C\equiv O:$$

Carbonic acid and the carbonates. A solution of carbon dioxide in water reacts slightly acidic with litmus. This is due to the presence of small quantities of carbonic acid, H_2CO_3 formed by the reaction between carbon dioxide and water :

$$CO_2+H_2O \rightleftharpoons H_2CO_3$$

The acid is unstable and has never been isolated. It is known only in aqueous solution. It is a weak dibasic acid and yields two series of salts : neutral salts which contain the CO_3^{-2} ion and acid salts which contain the HCO_3^- ion.

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^{-1}$$
$$HCO_3^{-1} \rightleftharpoons H^+ + CO_3^{-2}$$

The neutral salts containing the CO_3^{-2} ion are called carbonates and the acid salt containing the HCO_3^{-1} ion, the bicarbonates or hydrogen carbonates.

(i) **Carbonates.** Carbonates may be prepared by the action of carbon dioxide on basic oxides in the presence of a trace of moisture :

$$CaO+CO_2=CaCO_3$$
$$Na_2O+CO_2=Na_2CO_3$$

They are also produced by the action of carbon dioxide on the solutions of hydroxides :

$$Ca(OH)_2+CO_2=CaCO_3+H_2O$$
$$2NaOH+CO_2=Na_2CO_3+H_2O$$

They are also obtained by the double decomposition reaction between the soluble salts of carbonic acid and the salts of other acids :

$$BaCl_2+Na_2CO_3=BaCO_3+2NaCl$$
$$CaCl_2+Na_2CO_3=CaCO_3+2NaCl$$

Barium carbonate and calcium carbonate are obtained in the form of white precipitates.

When heated more or less strongly, all the carbonates except those of alkali metals decompose into carbon dioxide and the oxides of the corresponding metals :

$$MgCO_3=MgO+CO_2$$
$$CaCO_3=CaO+CO_2$$

Among the most common carbonates, only potassium, sodium and ammonium carbonates are soluble in water. The solutions of sodium and potassium carbonates are strongly alkaline owing to hydrolysis :

$$Na_2CO_3+H_2O \rightleftharpoons NaOH+NaHCO_3$$

Their solutions can be titrated directly with acids. If phenolphthalein is used as indicator, it becomes colourless at the half-way stage, i.e., when carbonate is converted into bicarbonate since bicarbonate is neutral to phenolphthalein :

$$2Na_2CO_3+H_2SO_4=Na_2SO_4+2NaHCO_3$$

But if methyl orange is used as an indicator, the end point is not indicated until all the carbonate have completely reacted with the acid used in the titration, forming the salt of the acid :

$$Na_2CO_3+H_2SO_4=Na_2SO_4+H_2O+CO_2$$

The carbonates of all metals react with acids liberating carbon dioxide and forming the salt of the acid :

$$Na_2CO_3+2HCl=2NaCl+H_2O+CO_2$$

(ii) **Bicarbonates.** The acid salts of carbonic acid of greatest practical importance are sodium bicarbonate, $NaHCO_3$ (baking soda) and potassium bicarbonate, $KHCO_3$. They are obtained as precipitates when carbon dioxide is passed into concentrated solution of the normal carbonates.

$$Na_2CO_3+H_2O+CO_2=2NaHCO_3$$
$$K_2CO_3+H_2O+CO_2=2KHCO_3$$

Other bicarbonates are very unstable so that they do not exist in the solid state. They can, however, be obtained in solution by the reaction between carbonic acid (CO_2+H_2O) with hydroxides, and carbonates.

$$CaCO_3+H_2O+CO_2=Ca(HCO_3)_2$$

On heating, all bicarbonates are decomposed to the corresponding normal carbonates, thus

$$Ca(HCO_3)_2=CaCO_3+H_2O+CO_2$$

All bicarbonates are soluble in water ; the bicarbonates of sodium and potassium are less soluble than their carbonates while the bicarbonates of alkaline-earth metals are soluble but their carbonates are insoluble. Bicarbonates are decomposed by acids in a manner similar to carbonates, e.g.,

$$2NaHCO_3+H_2SO_4=Na_2SO_4+2CO_2+2H_2O$$

Comparison of carbonates and bicarbonates. (i) On heating, all carbonates except those of sodium and potassium decompose into the metal oxide and carbon dioxide while bicarbonates decompose into normal carbonates and carbon dioxide.

(ii) Both the carbonates and the bicarbonates of the alkali metals are soluble in water, the carbonates being more soluble. Other metal carbonates are insoluble whereas their bicarbonates are generally more soluble.

(iii) Both carbonates and bicarbonates react with dil. HCl with effervescence of carbon dioxide.

(iv) When treated with mercuric chloride solution, soluble carbonates give an immediate brown precipitate of a basic mercuric carbonate, while soluble bicarbonates give the precipitate only on heating.

(v) When treated with a solution of magnesium sulphate, soluble carbonates give a white precipitate of magnesium carbonate while soluble bicarbonates give the precipitates only on boiling :

$$MgSO_4+Na_2CO_3=MgCO_3+Na_2SO_4$$

$$MgSO_4+2NaHCO_3=Mg(HCO_3)_2+Na_2SO_4 \text{ (in cold)}$$

$$Mg(HCO_3)_2\rightleftharpoons MgCO_3+H_2O+CO_2 \text{ (on boiling)}$$

APPENDIX

(1) To show that the allotropes of carbon consist entirely of the same element. A known weight of one allotrope of carbon is taken in a porcelain boat and heated strongly in a stream of dry pure oxygen in a glass tube. Carbon dioxide formed passes through the black copper oxide which oxidises any carbon monoxide which might be formed to carbon dioxide and is absorbed in solution of potassium hydroxide contained in U-tubes which were weighed previously. The increase in weight of the U-tubes gives the weight of carbon dioxide formed. The experiment is repeated with an equal weight of other allotropes of carbon and the same increase of weight in the U-tubes is observed in each case. Thus the same weight of carbon dioxide is formed when same weight of different allotropes of carbon are burnt in oxygen—a fact which is only possible if the different allotropes consist of the same element, carbon.

(2) **To prove that carbon monoxide and carbon dioxide contain carbon.** A piece of ignited magnesium is introduced into a jar of carbon dioxide when it continues to burn in the gas. Black carbon particles are separated and magnesium oxide is formed :

$$2Mg+CO_2=2MgO+C$$

The residue is treated with hot dilute hydrochloric acid when magnesium oxide dissolves, carbon being left undissolved. Carbon particles are filtered off, washed with water and then dried. They are then burnt in oxygen and the resulting gas turns lime-water milky. Hence, these black particles are carbon and they have come from carbon dioxide. Hence, carbon dioxide contains carbon.

In order to prove that carbon monoxide contains carbon, the gas is passed over red-hot cupric oxide taken in a hard-glass tube when carbon monoxide is oxidised to carbon dioxide. A piece of ignited magnesium is then introduced into the resulting gas when magnesium burns forming magnesium oxide with the separation of black particles. That these black particles are carbon is proved by the tests given above.

(3) **Conversion of carbon monoxide into carbon dioxide and vice-versa.** Carbon monoxide on burning in oxygen is converted to carbon dioxide. When carbon monoxide is passed over heated cupric oxide, lead oxide or zinc oxide, it is oxidised to carbon dioxide :

$$2CO+O_2=2CO_2\ ;\ CO+CuO=Cu+CO_2$$

When carbon dioxide is passed over red-hot carbon, it is reduced to carbon monoxide.

$$CO_2+C=2CO$$

The mutual conversion of carbon monoxide into carbon dioxide can be expressed by the following equation :

$$CO_2 \underset{\text{burning in oxygen}}{\overset{\text{red-hot carbon}}{\rightleftharpoons}} 2CO$$

(4) **Identification of CO_2 and SO_2 in a mixture of them.** The mixture of CO_2 and SO_2 is passed through acidified solution of

potassium dichromate when the solution turns green. This proves the presence of SO_2 in the mixture.

$$K_2Cr_2O_7+3SO_2+H_2SO_4=K_2SO_4+Cr_2(SO_4)_3+H_2O$$

Sulphur dioxide is absorbed in the solution while carbon dioxide remains unabsorbed.

The unabsorbed gas which comes out of the solution turns lime-water milky when passed into it. Hence, it is carbon dioxide. This proves the presence of carbon dioxide in the mixture.

(5) **Comparative study of carbon monoxide and carbon dioxide.**

Carbon monoxide	Carbon dioxide
(1) It is a colourless, odourless and nearly tasteless gas. The gas condenses to a colourless transparent liquid at −192°C.	It is a colourless, odourless gas with slightly sour taste. Under pressure and at ordinary temperature, it condenses to a colourless liquid.
(2) It is slightly soluble in water and does not react with water chemically. Under high pressure and high temperature it reacts with alkalis to form formates : $NaOH+CO=HCOONa$	It dissolves fairly readily in water to form carbonic acid : $H_2O+CO_2=H_2CO_3$
(3) It burns in air or oxygen with a bluish flame to form carbon dioxide : $2CO+O_2=2CO_2$ It is not a supporter of combustion.	It is non-combustible and ordinarily is not a supporter of combustion.
(4) In carbon monoxide the oxidation number of carbon is +2. Hence, it can be easily oxidised to carbon dioxide. For this reason, carbon monoxide is a reducing agent.	Carbon dioxide cannot act as reducing agent because in CO_2 carbon is in the highest state of oxidation, viz., +4. Carbon dioxide can act as a oxidising agent in reactions in which carbon of carbon dioxide changes its oxidation state from +4 to +2 or 0. For example, $CO_2+Zn=ZnO+CO$ $4K+3CO_2=2K_2CO_3+C$

Carbon monoxide	Carbon dioxide
(5) Carbon monoxide can form additive compounds such as carbonyl chloride, carbonyl sulphide, and metal carbonyls. $CO+Cl_2=COCl_2$; $CO+S=COS$; $Fe+5CO=Fe(CO)_5$	Carbon dioxide cannot form addition compounds.
(6) Carbon monoxide is absorbed by ammoniacal cuprous chloride solution.	Carbon dioxide is absorbed by NaOH, KOH, etc., solution.

EXERCISES

1. What are the allotropes of carbon ? Compare the physical properties of diamond and graphite. How would you prove that allotropes of carbon consist entirely of the same element ? How would you account for the extreme hardness of diamond ?

2. Describe the artificial production of graphite. How would you account for the following facts.

   (a) Graphite is a good conductor of electricity while diamond is not so.

   (b) Graphite is easily split into thin plates while diamond is split only with difficulty.

   How can synthetic diamond be made ? What are the uses of diamond and graphite ?

3. How does carbon occur in nature ? Describe with equations the typical chemical properties of carbon.

4. How would you prepare carbon monoxide in the laboratory ? Discuss the conditions that determine whether carbon and oxygen will form the monoxide or the dioxide.

   Under what conditions does carbon monoxide react with alkalis ? Discuss the reaction of CO with Cl_2, N_2 and the haemoglobin.

5. How is carbon monoxide converted into carbon dioxide and carbon dioxide into carbon monoxide ?

6. What is the physiological effect of CO on our bodies ? "Carbon monoxide is a good reducing agent while carbon dioxide does not so serve."—Explain.

7. Describe the laboratory preparation of carbon dioxide. Why is HCl and not H_2SO_4 used in the preparation of carbon dioxide from marble ?

8. Give an account of the properties and industrial uses of carbon dioxide. What is "dry ice" ? Why does dry ice sublime and not melt at one atmosphere pressure ?

9. What function does carbon dioxide play in the life processes of plants and animals ? Why is solid carbon dioxide used as a refrigerating

agent? Write equation for the reaction that takes place when carbon dioxide is bubbled through lime water until lime water again becomes clear.

10. What is the action of steam on red-hot carbon. How is this reaction adopted for industrial use? Name the constituents of water gas.

11. What principles are involved in extinguishing a fire? Describe the operation and chemistry of soda-acid type fire-extinguishers.

12. Describe the manufacture of coke.

13. Explain what is meant by the terms combustion and oxidation. [C. U., '57]

14. Explain with equations what happens when:

(i) calcium carbide is treated with water.

(ii) air is passed through a bed of red-hot coke.

(iii) steam is passed through a bed of red-hot coke.

(iv) carbon dioxide is passed into KOH solution.

15. Explain the following statements:

(a) Diamond and graphite are allotropic forms of carbon. One is hard and resistant to attack by chemicals while the other is soft and less resistant to attack by chemicals. [I. S. C. (12), '78]

(b) Carbon monoxide is a good reducing agent while carbon dioxide is a good oxidising agent.

(c) Charcoal floats on water although its specific gravity is greater than that of water.

(d) Carbonic acid is a di-basic acid.

16. How would you prove that carbon monoxide and carbon dioxide contain carbon.

17. (a) How would you identify carbon monoxide and hydrogen in a mixture of them?

(b) How would you detect the presence of carbon dioxide and nitrogen in the mixture of them?

(c) How would you identify carbon dioxide and sulphur dioxide in a mixture of them?

18. Compare the properties of carbon monoxide with those of carbon dioxide.

19. What happens when

(a) a mixture of carbon monoxide and chlorine is exposed to sunlight.

(b) carbon monoxide is passed through sodium hydroxide solution under pressure.

(c) carbon monoxide is passed through ammoniacal cuprous chloride solution.

(d) steam is passed over red-hot coke.

(e) carbon monoxide is passed over heated cupric oxide.

(f) carbon dioxide is passed through lime-water.

(g) carbon dioxide is passed through sodium hydroxide solution.

(h) a burning magnesium ribbon is placed into a jar of carbon dioxide. [H. S., '71]

CHAPTER VIII

PHOSPHORUS AND ITS COMPOUNDS

Atomic weight, 30·975 Atomic number, 15

Electronic configuration, $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$

Phosphorus was discovered in 1674 by the German alchemist Brand. In the course of his search for the philosopher's stone, a substance that was thought capable of changing baser metals to gold, he distilled a mixture of sand and the residue left on evaporation of urine and obtained a solid substance which had the property of glowing in the dark. To it, he gave the name, phosphorus (*phos, light ; phero, I carry*). Phosphorus was obtained in 1771 by Scheele from bone ash. The elementary nature of phosphorus was first recognised by Lavoisier.

Phosphorus does not occur free in nature because of its reactivity in air. It, however, is widely distributed in the form of phosphates. Some of the minerals containing phosphorus are : chlorapatite, $3Ca_3(PO_4)_2$, $CaCl_2$; fluorapatite, $3Ca_3(PO_4)_2$, CaF_2 ; phosphorite and sombrerite, $Ca_3(PO_4)_2$; vivianite, $Fe_3(PO_4)_2$, $8H_2O$; wavelite, $4AlPO_4$, $2Al(OH)_3$, $9H_2O$. The most important of these is the mineral phosphorite commonly called phosphate rock. Monazite is a valuable mineral which contains the phosphates of rare earth metals.

The animal body contains complex organic phosphorus compounds in the nerves, muscles and brains ; bones and teeth are made up largely of calcium phosphate and calcium carbonate. Phosphorus is thus essential to the growth of plant and animal. A growing child needs foods which contain phosphorus and calcium. Milk, egg, seeds such as peas and beans, and wheat grains also contain combined phosphorus.

Preparation of phosphorus. (i) Retort Process (Old process). In this process, phosphorus is manufactured largely by heating bone ash with sulphuric acid. The bones contain calcium phosphate (about 58%), a little calcium carbonate, fats, gelatin, and nitrogenous organic matters. The bones are digested with benzene, or carbon disulphide to remove fats and greasy matters. "Degreased bones" thus obtained are then digested with water under pressure to remove gelatin. The "degelatinised bones" ramaining are then subjected to destructive distillation in a closed vessel when bone-black is formed. Bone-black on being heated in air gives bone-ashes. Bone ash contains mainly calcium phosphate (about 80%).

Powdered bone ash is heated with hot and fairly concentrated sulphuric acid when insoluble calcium sulphate and phosphoric acid are formed :

$$Ca_3(PO_4)_2 + 3H_2SO_4 = 3CaSO_4 + 2H_3PO_4$$

Calcium sulphate is filtered off and the filtrate containing phosphoric acid is evaporated to a syrup. Phosphoric acid on heating loses water to give metaphosphoric acid :

$$H_3PO_4 = HPO_3 + H_2O$$

The metaphosphoric acid is then mixed with powdered coke ; the mixture is distilled in fire-clay retorts at a bright-red heat. Phosphorus formed vaporises and the vapour is led under water when it condenses as white phosphorus and the mixture of CO and H_2 escapes.

$$4HPO_3 + 12C = P_4 + 2H_2 + 12CO$$

This process of manufacturing phosphorus is now obsolete.

Preparation of bone-black and bone-ash. Bones contain fat, gelatin, nitrogenous compounds and small amount of calcium carbonate.

The bones are cut into pieces and boiled with water and filtered. They are then digested with carbon disulphide or carbon tetrachloride to remove fats and greasy substances. The pieces of degreased bones thus obtained are then heated in superheated steam to remove gelatin. They are then subjected to destructive distillation in a closed vessel in absence of air. The black mass that remains after distillation is called bone-black or bone-charcoal. When bone-charcoal is heated strongly in air, bone-ash is formed. Bone-ash contains 80% calcium phosphate and is an important source of phosphorus.

The electric furnace process. Phosphorus is now made by heating natural phosphate, $Ca_3(PO_4)_2$ with sand and coke without access of air in special furnaces by means of electric current. In order to understand the reaction, calcium phosphate is conceived as a compound of calcium oxide and phosphoric anhydride $[Ca_3(PO_4)_2 = 3CaO, P_2O_5]$. At high temperatures, silica, SiO_2 on account of its nonvolatility displaces phosphorus pentoxide from $Ca_3(PO_4)_2$ and combines with calcium oxide forming calcium silicate, $CaSiO_3$. Phosphorus pentoxide is then reduced by coke to elemental phosphorus :

$$P_2O_5.3CaO + 3SiO_2 = 3CaSiO_3 + P_2O_5 ; \quad P_2O_5 + 5C = 2P + 5CO$$

By adding up these two equations, we get the over-all reaction :

$$Ca_3(PO_4)_2 + 3SiO_2 + 5C = 3CaSiO_3 + 2P + 5CO$$

The phosphorus liberated leaves the furnace as vapour and is condensed under cold water to white phosphorus.

A mixture of mineral phosphate, sand and coke is introduced into a closed electric furnace through hopper by a screw conveyer.

The furnace is made up of brick-work and is provided with an outlet above for the escape of gases and phosphorus vapours and a slag hole below. Two carbon electrodes through which an electric arc is struck are fixed near the bottom of the furnace. By passing electric current through the electrodes the furnace is heated to very high temperatures when the reaction takes place and phosphorus, carbon monoxide and calcium silicate are formed. Phosphorus liberated vaporises and the mixture of phosphorus vapours and carbon monoxide leaves the furnace through the outlet at the top and is bubbled under cold water where phosphorus vapours condense as white phosphorus and carbon monoxide passes out. The calcium silicate collects at the bottom of the furnace as a liquid slag which is drawn off at intervals.

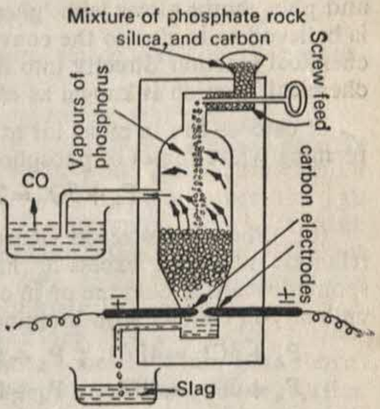


Fig. 8.1

Purification. Crude phosphorus thus obtained is not pure and contains carbon, sand and other impurities. In order to purify it, the crude phosphorus is melted under hot water and stirred with a mixture of sulphuric acid and potassium dichromate when some of the impurities are oxidised and pass into the solution and other impurities separate and rise as a scum. The liquid phosphorus is then filtered through canvas. Colourless phosphorus is finally cast into sticks and is stored and transported under water as it inflames at very low temperatures in contact with air.

Allotropes of phosphorus. Phosphorus exists in several allotropic modifications. The most important of these are white (or yellow) phosphorus and red phosphorus.

(i) **White phosphorus.** White phosphorus is obtained when phosphorus vapours are cooled rapidly. It is a translucent, waxy, white, crystalline solid. Above 15°C, it softens and can easily be cut with a knife. It melts at 44·2°C and begins to boil at 280·5°C.

White phosphorus is scarcely solube in water but it is readily solube in benzene, olive oil, carbon disulphide, sulphur chloride and phosphorus trichloride. Carbon disulphide dissolves nine times its weight of phosphorus.

It sublimes at room temperature ; the vapours of phosphorus are very poisonous. In the vapour form below 1000°C, the phosphorus molecule consists of four atoms. At 1600°C the vapour is dissociated slightly forming a few per cent of the diatomic molecule.

$$P_4 \rightleftharpoons 2P_2$$

Chemical properties : Because of its reactivity, white phosphorus enters into wide variety of reactions with metals, non-metals and compounds.

(i) **Reaction with non-metals.** (a) When white phosphorus is exposed to air, it undergoes spontaneous oxidation forming white fumes of phosphorus trioxide. Some ozone is formed simultaneously and phosphorus glows with ghostly green light. The light evolved is believed to be due to the conversion of some of the energy of the chemical reaction directly into light. Such a production of light by chemical reaction is known as *chemiluminescence.*

It catches fire in moist air at 30°C and burns with a white flame forming white fumes of phosphorus pentoxide :

$$P_4+5O_2=2P_2O_5$$

(b) Phosphorus reacts vigorously with halogens forming first the trihalide and with excess of halogen, the pentahalide. It burns spontaneously in chlorine or in contact with solid iodine. It explodes violently in contact with bromine.

$$P_4+6Cl_2=4PCl_3\ ;\ P_4+10Cl_2=4PCl_5\ ;\ P_4+6I_2=4PI_3$$

$$P_4+6Br_2=4PBr_3\ ;\ P_4+10Br_2=4PBr_5$$

(c) When heated with sulphur, white phosphorus reacts explosively. By using the proper quantities of the two elements, sulphides such as P_4S_3, P_4S_5, P_4S_7 and P_4S_{10}, or P_2S_5 can be prepared. Phosphorus does not react directly with hydrogen but hydrides of phosphorus can be prepared indirectly.

(ii) **Reaction with metals.** Phosphorus unites directly with many metals to form metallic phosphides. For example, if sodium is cautiously heated with white phosphorus, sodium reacts with phosphorus with a bright flash forming sodium phosphide, Na_3P.

(iii) **Reaction with compounds.** (a) White phosphorus reacts with alkali forming phosphine and hypophosphite.

$$P_4+3NaOH+3H_2O=PH_3+3NaH_2PO_2$$

(b) White phosphrus is an active reducing agent. It is oxidised by nitric acid to phosphoric acid.

$$P_4+10HNO_3+H_2O=4H_3PO_4+5NO+5NO_2$$

(c) White phosphorus reacts with copper sulphate solution yielding metallic copper and black copper phosphide :

$$3P+3CuSO_4+6H_2O=Cu_3P+2H_3PO_3+3H_2SO_4$$

$$2P+5CuSO_4+8H_2O=5Cu+5H_2SO_4+2H_3PO_4$$

Silver nitrate also reacts with phosphorus forming silver phosphide Ag_3P.

If phosphorus is accidentally dropped on the hand, it may be removed by washing with copper sulphate solution.

(ii) **Red phosphorus. Conversion of white phosphorus to red phosphorus.** White phosphorus is metastable at ordinary temperature and gradually changes into the red form. The transformation is accompanied by the evolution of heat.

$$\text{P (white)} = \text{P (red)} + 4 \text{ kcal.}$$

Hence, the red phosphorus is more stable than the white phosphorus.

Red phosphorus is obtained by heating white phosphorus to about 250°C in the absence of air ; the transformation is catalysed by a trace of iodine. On the industrial scale, white phosphorus and a little iodine are taken in an iron pot closed with a cover through which passes an upright iron pipe. The iron pipe is open at each end to prevent the development of pressure inside the pot. The pot is heated carefully to 240°C. A very small part of phosphorus burns, removing oxygen from the air initially present in the pot, after which no oxygen enters into pot by the long pipe and hence further oxidation ceases. Under these conditions molten white phosphorus changes rapidly into solid red phosphorus. When the conversion is complete, the product is ground with water and boiled with a solution of caustic soda to remove any oxide formed as well as any unconverted white phosphorus. The red phosphorus is then repeatedly washed with hot water and dried with steam.

Conversion of red phosphorus to white phosphorus. A quantity of red phosphorus is taken in a hard glass tube fitted with two rubber stoppers through which pass two smaller tubes. A stream of carbon dioxide or nitrogen is passed through the tube when air is displaced from the tube. Red phosphorus is then heated in a slow current of carbon dioxide or nitrogen (to prevent oxidation of phosphorus) when red phosphorus vaporises and the vapours are condensed on the cooler part of the tube as crystals of white phosphorus.

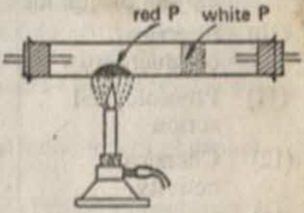


Fig. 8.2

Properties of red phosphorus. Red phosphorus is the stable form of phosphorus at ordinary temperatures. It is reddish violet crystalline solid which sublimes on heating (sublimation temperature, 416°C). The vapour condenses into white phosphorus. It is insoluble in carbon disulphide and is not poisonous.

Chemically, red phosphorus is less active than white phosphorus. When heated in air to about 260°C, red phosphorus ignites forming phosphorus pentoxide. It reacts with halogens and sulphur but less vigorously than white phosphorus. Thus, red phosphorus burns if heated in an atmosphere of chlorine whereas white phosphorus takes fire spontaneously in the gas. It does not react with alkalis.

The principal differences between red and white phosphorus are summarised in table 8.1.

Table 8.1. Comparison of white and red phosphorus.

Property	White phosphorus	Red phosphorus
(1) Colour	Almost colourless	Reddish violet
(2) Odour	Garlic smell	Odourless
(3) Physical state at S.T.P.	Crystalline solid	Crystalline solid
(4) Specific gravity	1·82	2·2
(5) Stability	Metastable at ordinary temperature.	Stable
(6) Melting point.	44·1°C	597°C
(7) Boiling point	280·5°C	Very high
(8) Solubility in water.	Almost insoluble	Insoluble
(9) Solubility in carbon disulphide	Soluble	Insoluble
(10) Electrical conductivity	Very feeble conductor	Feeble conductor
(11) Physiological action	Very poisonous	Non-poisonous
(12) Chemical activity	Very reactive	Less reactive
(13) Ignition temperature in air	30°C	260°C
(14) Action of air	It undergoes spontaneous oxidation with green glow or chemiluminescence	It does not glow, i. e., no chemiluminesence
(15) Action of chlorine	Catches fire spontaneously	Catches fire if heated
(16) Action of hot sodium hydroxide	Reacts giving off phosphine	No reaction

(iii) **Black phosphorus.** Metallic or black phosphorus is obtained by heating white phosphorus at 220°C under high pressure, about 12,000 atmospheres. In outward appearance, it resembles graphite. It is greasy to touch and is a fairly good conductor of electricity. Its specific gravity is 2·7 and is much heavier than other modifications of phosphorus. It is chemically slightly less reactive than red phosphorus and ignites in air at 490°C.

(iv) **Scarlet phosphorus.** When a solution of red phosphorus in phosphorus tribromide is exposed to light or boiled for some time, scarlet phosphorus separates out as a scarlet red powder.

(v) **Violet phosphorus.** Red phosphorus dissolves in molten lead. If the solution is allowed to solidify and if lead is dissolved, crystals of violet phosphorus remain. Violet phosphorus has chemical properties similar to those of red phosphorus. Red and violet phosphorus are believed to be chemically identical but differ only in crystal size.

Uses of phosphorus. (i) The important use of phosphorus is in the manufacture of phosphate salts to be used as fertilisers.

(ii) The chief field of application of phosphorus is the manufacture of matches. White phosphorus is not used for this purpose because of the poisonous nature of phosphorus vapour. Ordinary matches are now made by dipping the ends of the match sticks into paraffin and then into a wet mixture of phosphorus sulphide (P_4S_3), potassium chlorate or lead dioxide and glue. Friction produces sufficient heat to ignite P_4S_3 which in turn ignites the head of the stick and then the wood. In the safety matches, the head of the stick contains a mixture of potassium chlorate and antimony sulphide and the side of the match box is coated with a mixture of red phosphorus, powdered glass and glue. Heat which is produced in the friction vaporises a trace of red phosphorus which ignites and sets fire to the head of the match stick.

(iii) Phosphorus is employed in the manufacture of phosphor-bronzes and rat poison.

(iv) It is also used for military purposes. White phosphorus is used to fill smoke screen shells and hand grenades.

Hydrides of Phosphorus

Phosphorus forms three compounds with hydrogen, viz., gaseous hydrogen phosphide PH_3 called phosphine; liquid hydrogen phosphide, P_2H_4, and solid hydrogen phosphide, $P_{12}H_6$.

Phosphine, PH_3.

Phosphine was first obtained by Gengembre in 1783 by boiling white phosphorus with sodium hydroxide solution.

Preparation. Phosphine cannot be prepared by the direct union of phosphorus and hydrogen. It can be prepared by the following methods:

(i) **From white phosphorus and KOH or NaOH. Laboratory preparation.** Phosphine can be prepared by boiling white phosphorus with concentrated solution of sodium hydroxide. Sodium hypophosphite is formed at the same time.

$$P_4+3NaOH+3H_2O=3NaH_2PO_2+PH_3$$

Phosphine formed in this way is not pure but it contains hydrogen and the vapours of liquid hydrogen phosphide, P_2H_4 which are generated by the reactions :

$$2P+2NaOH+2H_2O=2NaH_2PO_2+H_2$$

$$6P+4NaOH+4H_2O=4NaH_2PO_2+P_2H_4$$

A mixture of 30—40 per cent solution of sodium hydroxide and few pieces of white phosphorus are taken in a flask fitted with a delivery tube and an inlet tube dipping in the solution. The free end of the delivery tube is dipped into water contained in a trough. A current of hydrogen or coal gas is first led through the apparatus by the inlet tube to drive out the air inside the flask. Air is removed in order to avoid explosion which would occur by the spontaneous ignition of a mixture of phosphine and air. The mixture in the flask is then slowly heated and phosphine evolved passes through the delivery tube. As each drop of the gas rises up out of the water, it catches fire spontaneously producing rings of white smokes of phosphorus pentoxide. Pure phosphine is not spontaneously inflammable in air ; the spontaneous inflammability of the gas thus prepared is due to the presence of P_2H_4. P_2H_4 is removed from the gas by passing it through a tube immersed in a freezing mixture when P_2H_4 condenses and phosphine passes out and is collected by the displacement of water. Phosphine thus collected no longer inflames in contact with air.

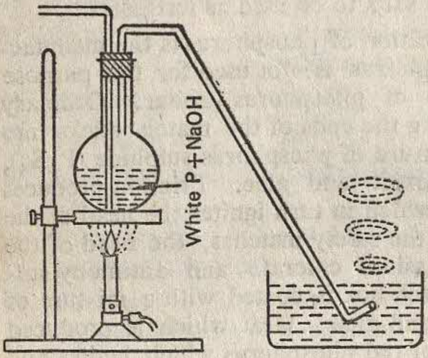


Fig. 8.3

(ii) **From phosphides of active metals.** Phosphine may be formed by the action of acidified water on a metallic phosphide

$$Ca_3P_2+6HCl=3CaCl_2+2PH_3$$

Phosphine thus formed contains P_2H_4 and is spontaneously inflammable in air.

Phosphine is also formed by the action of dilute sulphuric acid on aluminium phosphide.

$$2AlP+3H_2SO_4=Al_2(SO_4)_3+2PH_3$$

(iii) **From phosphonium iodide.** Pure phosphine is prepared by warming phosphonium iodide with potassium hydroxide solution.

$$PH_4I + KOH = KI + H_2O + PH_3$$

Phosphine evolved is dried and collected over mercury.

Properties. (A) Physical properties. Phosphine is a colourless gas. It has an odour of rotten fish and is poisonous. Its melting point is −132°C and boiling point is −86°C. It is slightly soluble in water and the solution is neutral to litmus.

(B) Chemical properties : (i) **Stability to heat.** Phosphine is decomposed completely into hydrogen and red phosphorus either by heating to 440°C or sparking.

(ii) It burns in air forming phosphorus pentoxide and water.

$$2PH_3 + 4O_2 = P_2O_5 + 3H_2O$$

If a mixture of pure phosphine and oxygen or air is rarefied, a violent explosion occurs.

(iii) Phosphine reacts with all the halogens liberating a great amount of heat.

$$PH_3 + 4Cl_2 = 3HCl + PCl_5$$

A mixture of phosphine with nitrous oxide, when sparked, explodes.

$$2PH_3 + 8N_2O = P_2O_5 + 3H_2O + 8N_2$$

(iv) Phosphine is slightly basic and reacts with hydrogen halides forming phosphonium halide. Thus, it reacts with hydrochloric acid forming phosphonium chloride.

$$PH_3 + HCl = PH_4Cl$$

Similarly, with hydriodic acid and hydrobromic acid, the reactions are :

$$PH_3 + HI = PH_4I\ ;\quad PH_3 + HBr = PH_4Br$$

(v) Because of the decomposition of phosphine into phosphorus and hydrogen when heated, phosphine acts as a very powerful reducing agent. Thus, it precipitates silver and gold from solutions of their salts.

$$PH_3 + 6AgNO_3 = Ag_3P,\ 3AgNO_3 + 3HNO_3$$

$$Ag_3P,\ 3AgNO_3 + 3H_2O = 6Ag + 3HNO_3 + H_3PO_3$$

Similarly, when passed into the solutions of copper sulphate, mercuric chloride, etc., phosphine precipitates the phosphides of the metals.

$$3CuSO_4 + 2PH_3 = 3H_2SO_4 + Cu_3P_2$$

$$3HgCl_2 + 2PH_3 = 6HCl + Hg_3P_2$$

(vi) Like ammonia it combines with some chlorides such as aluminium chloride, stannic chloride and cuprous chloride.

$$AlCl_3 + PH_3 = AlCl_3, PH_3$$

$$CuCl + PH_3 = CuCl, PH_3$$

Absorbents. The gas is absorbed by (i) bleaching powder solution and (ii) silver sulphate solution.

Tests. The gas is detected by the following tests :

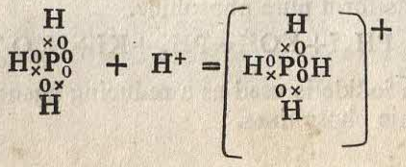
(i) its smell of decaying fish (ii) a black precipitate of copper phosphide is obtained when the gas is passed through copper sulphate solution. (iii) a black precipitate is obtained when the gas is passed through silver nitrate solution.

Comparison of phosphine and ammonia. Nitrogen and phosphorus are placed in the same group in the periodic table. Phosphorus forms the hydride, phosphine, whose formula is analogous to that of ammonia. The principal similarities and differences between ammonia and phosphine are given below.

Ammonia, NH_3	Phosphine, PH_3
(1) A colourless gas lighter than air.	A colourless gas heavier than air.
(2) It possesses a pungent smell.	It possesses the smell of rotten fish.
(3) It is non-poisonous.	It is highly poisonous.
(4) Highly soluble in water ; the solution is basic in character.	Sparingly soluble in water ; the solution is neutral in character.
(5) It is not supporter of combustion ; it burns in excess of air or oxygen forming nitrogen : $4NH_3 + 3O_2 = 2N_2 + 6H_2O$	It is not supporter of combustion. It burns in air forming phosphorus pentoxide : $2PH_3 + 4O_2 = P_2O_5 + 3H_2O$
(6) It reacts with excess of chlorine to form nitrogen trichloride and hydrogen chloride. $NH_3 + 3Cl_2 = NCl_3 + 3HCl$ When ammonia is in excess nitrogen is formed. $8NH_3 + 3Cl_2 = N_2 + 6NH_4Cl$	It spontaneously inflames and burns in chlorine gas, forming phosphorus pentachloride. $PH_3 + 4Cl_2 = PCl_5 + 3HCl$

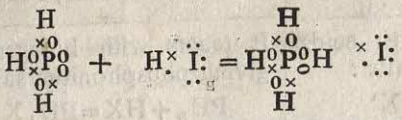
Ammonia, NH_3	Phosphine, PH_3
(7) It reacts with acids forming ammonium salts : $NH_3+HX=NH_4X$ (where $X=Cl, Br, I$)	It reacts with halogen acids giving phosphonium salts. $PH_3+HX=PH_4X$ (where $X=Cl, Br, I$)
(8) It is a reducing agent only at high temperatures ; it reduces cupric oxide or lead monoxide to metals at high temperatures. $3CuO+2NH_3=3Cu+3H_2O+N_2$	It is a strong reducing agent ; it precipitates silver and gold from solutions of their salts. $PH_3+6AgNO_3=Ag_3P, 3AgNO_3+3HNO_3$ $Ag_3P, 3AgNO_3+3H_2O=6Ag+3HNO_3+H_3PO_3$
(9) When the gas is passed in the solutions of the salts of metals, metallic hydroxides are usually precipitated.	The gas when passed into a solution of copper sulphate, mercuric chloride, etc., metallic phosphides are precipitated.
(10) The gas dissociates into its elements at very high temperatures or by electric sparks.	The gas decomposes into its elements at 440°C or by electric sparks.
(11) It can be prepared by heating the ammonium salts of halogen acids with sodium hydroxide. $NH_4Cl+NaOH=NH_3+NaCl+H_2O$	It can be prepared by heating the ammonium salts of halogen acids : $PH_4I+NaOH=NaI+H_2O+PH_3$
(12) Hydrolysis of nitrides of active metals yields ammonia. $Mg_3N_2+6H_2O=2NH_3+3Mg(OH)_2$	Hydrolysis of phosphides of active metals yields phosphine. $Ca_3P_2+6H_2O=3Ca(OH)_2+2PH_3$

Phosphonium compounds. In the molecule of phosphine, two electrons of phosphorus remain unshared. These electrons may be used to form coordinate covalent union with hydrogen ions forming phosphonium ion :



$$\begin{array}{c}H\\ {\scriptstyle\times\circ}\\ H{}^{\circ}_{\times}P{}^{\circ}_{\circ}\\ {\scriptstyle\circ\times}\\ H\end{array} + H^+ = \left[\begin{array}{c}H\\ {\scriptstyle\times\circ}\\ H{}^{\circ}_{\times}P{}^{\circ}_{\circ}H\\ {\scriptstyle\circ\times}\\ H\end{array}\right]^+$$

This is analogous to the formation of ammonium ion. Thus, with hydriodic acid, phosphine forms phosphonium iodide :



$$\mathrm{H}^{\circ}_{\times}\underset{\underset{\mathrm{H}}{\circ\times}}{\overset{\overset{\mathrm{H}}{\times\circ}}{\mathrm{P}}}{}^{\circ}_{\circ} + \mathrm{H}^{\times}_{\cdot}\ddot{\underset{\cdot\cdot}{\mathrm{I}}}: = \mathrm{H}^{\circ}_{\times}\underset{\underset{\mathrm{H}}{\circ\times}}{\overset{\overset{\mathrm{H}}{\times\circ}}{\mathrm{P}}}{}^{\circ}_{\circ}\mathrm{H}\quad {}^{\times}_{\cdot}\ddot{\underset{\cdot\cdot}{\mathrm{I}}}:$$

(phosphonium iodide)

In these reactions, phosphine acts as a weak base and the products are known as phosphonium compounds.

When dry phosphine is brought into contact with dry halogen hydracids at high pressures, the gases unite forming phosphonium salts :

$$PH_3+HX=PH_4X \text{ (where } X=Cl, Br, I \text{)}$$

Phoshonium chloride is obtained as white crystals by cooling a mixture of phosphine and dry hydrogen chloride to −35°C or by compressing the mixture at 15°C :

$$PH_3+HCl=PH_4Cl$$

Phosphonium bromide is more stable and is obtained as crystals by passing a mixture of phosphine and hydrogen bromide into a cooled flask.

Phosphonium iodide is fairly stable and may be obtained by mixing phosphine and hydrogen iodide at ordinary temperature and pressure. It is best prepared by dissolving phosphorus and iodine in carbon disulphide in a glass retort and then distilling off the carbon disulphide. The residue is then treated drop by drop by the exact quantity of water indicated by the equation given below. Phosphonium iodide sublimes and is deposited as white crystals in a long air-cooled tube attached to the neck of the retort.

$$9P+5I+16H_2O=5PH_4I+4H_3PO_4$$

Phosphonium salts undergo thermal dissociation into phosphine and the hydracid.

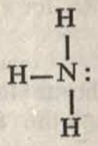
$$PH_4I \rightleftharpoons PH_3+HI$$

The dissociation of phosphonium iodide takes place at 60°C ; other salts dissociate at still lower temperature. These salts are easily decomposed into phosphine and hydracids by the action of water. This suggests that phosphine does not react with water to form phosphonium hydroxide ; with potassium or sodium hydroxide, phosphonium salts form pure phosphine.

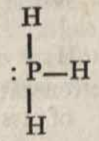
$$PH_4I+KOH=PH_3+KI+H_2O$$

Phosphonium iodide is used as a reducing agent and in the preparation of organic phosphines.

Explanation of basic properties of ammonia and phosphine. In the molecule of ammonia, the nitrogen atom contains a lone pair of electron. Similarly, in the molecule of phosphine, the phosphorus atom contains a lone pair of electron.



$$\begin{array}{ccc} & H & \\ & | & \\ H- & N & : \\ & | & \\ & H & \end{array}$$



$$\begin{array}{ccc} & H & \\ & | & \\ : & P & -H \\ & | & \\ & H & \end{array}$$

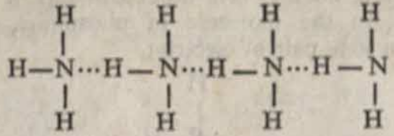
Therefore, the basic properties of ammonia and phosphine arise as a result of the tendency of nitrogen and phosphorus atom to share their lone pair of electrons. These electrons are used to form co-ordinate covalent union with hydrogen ions. Consequently, they act as bases.

Nitrogen is highly electronegative and the electronegativity of nitrogen is much greater than that of phosphorus. Hence, the electrons of the H—N bonds are strongly shifted from the hydrogen to the nitrogen and consequently, electron-density on nitrogen atom becomes high. On the other hand, because of low electronegativity of phosphorus (electronegativity of phosphorus and hydrogen is almost the same), the electron-density on phosphorus atom in phosphine molecule is much less than that on nitrogen atom in ammonia molecule. Consequently, nitrogen atom in ammonia has a greater tendency to share its lone pair of electrons than phosphorus atom in phosphine. Hence, ammonia is more basic than phosphine.

Explanation of some properties of ammonia and phosphine from electronic point of view. (a) Although ammonia is a covalent compound, it is highly soluble in water. On the other hand, phosphine is sparingly soluble in water. The high solubility of ammonia in water is due to the fact that ammonia forms hydrogen bonds with water. Nitrogen is highly electronegative and consequently the electrons of the H—N bond are strongly shifted from hydrogen to the nitrogen in ammonia molecule. For this reason, the hydrogen atoms in ammonia must be relatively positive. It is this partial positive charge which enables hydrogen to attract highly electronegative oxygen atoms of water to form hydrogen bond.

Because of low electronegativity of phosphorus atom, phosphine is unable to form hydrogen bond with water. This explains its insolubility in water.

(b) Because of high electronegativity of nitrogen, the electrons of the H—N bonds in ammonia molecule are strongly shifted from the hydrogen to the nitrogen, and consequently, the hydrogen atoms become relatively positive. Hence, ammonia molecules can associate through the formation of hydrogen bonds.



$$H{-}N\cdots H{-}N\cdots H{-}N\cdots H{-}N$$

Due to the low electronegativity of phosphorus the phosphine molecule is incapable of associating through the formation of hydrogen bonds.

Oxides of phosphorus

Phosphorus forms three oxides which are listed in table 8.2. Of these phosphorus tetroxide is not included in the syllabus and hence it is not discussed here.

Table 8.2

Name	Formula	Oxidation number of phosphorus
Phosphorous oxide or phosphorus trioxide.	P_2O_3 or P_4O_6	+3
Phosphorus tetroxide	P_2O_4	+4
Phosphorus pentoxide	P_2O_5 or P_4O_{10}	+5

Phosphorous oxide or phosphorus trioxide. P_2O_3 or P_4O_6. **Preparation.** Phosphorus trioxide, P_2O_3, is prepared by the slow oxidation of phosphorus or by burning phosphorus in a limited supply of air.

$$P_4+3O_2=2P_2O_3$$

A small amount of phosphorus pentoxide is also formed simultaneously.

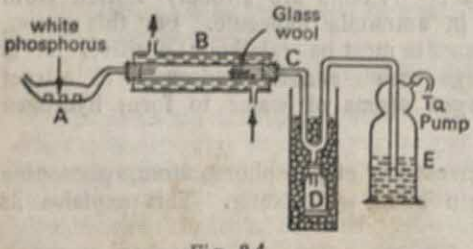


Fig. 8.4

Some white phosphorus is placed in a glass tube (A). The tube is connected with the metal condenser (B) which is surrounded by water at 60°C. The condenser is fitted to a U-tube immersed in a freezing mixture ; a plug of glass-wool is placed in the condenser near the U-tube. The U-tube is connected through wash-bottle (E) containing concentrated sulphuric acid with a water-pump. Phosphorus in the tube is ignited and a slow stream of air is drawn through the apparatus by means of the water-pump. The vapours of the oxides formed pass through the condenser and then through the glass wool. The phosphorus pentoxide is arrested by the glass wool and phosphorus trioxide passes into the U-tube where it is condensed as a white crystalline mass. The concentrated sulphuric acid in the bottle protects the product from moisture. The solid phosphorus trioxide in the U-tube on warming melts and the liquid is run in the bottle (D).

Properties. Phosphorus trioxide is a white crystalline solid which melts at 22·5°C and boils at 173·1°C. It is very poisonous and has unpleasant acid smell. Its vapour density corresponds to the formula P_4O_6.

Phosphorus trioxide reacts with oxygen at ordinary temperature forming phosphorus pentoxide ; when it is heated in presence of air, it bursts into flame.

$$P_2O_3+O_2=P_2O_5$$

It dissolves slowly in cold water forming phosphorous acid of which it is the anhydride.

$$P_2O_3+3H_2O=2H_3PO_3$$

When phosphorus trioxide is added to hot water, it undergoes simultaneous oxidation and reduction usually referred to auto-oxidation reduction, forming phosphine and phosphoric acid.

$$2P_2O_3+6H_2O=3H_3PO_4+PH_3$$

In chlorine, it ignites spontaneously forming phosphorus oxychloride $POCl_3$.

Phosphorus pentoxide, P_2O_5. Preparation. When phosphorus is burnt in excess of dry air or oxygen, dense white clouds of phosphorus pentoxide are obtained. The fumes condense as a voluminous powder upon the sides of the cold vessel. The white powder of phosphorus pentoxide thus obtained is usually contaminated with traces of P_2O_3 and metaphosphoric acid $(HPO_3)_n$. These impurities are removed by heating the powder to 600°—700°C in an iron tube attached to a glass tube through which dry oxygen is passing at a fairly rapid rate. The pentoxide is vaporised and condenses in the glass tube.

$$P_4+5O_2=2P_2O_5$$

Properties. Phosphorus pentoxide is a white powder and is extremely hygroscopic. It sublimes at 250°C. When heated under pressure, it melts at 800°C and on cooling it solidifies to a vitreous mass. Its vapour density corresponds to the formula P_4O_{10}.

It reacts with cold water with a hissing sound and evolution of much heat, forming metaphosphoric acid.

$$P_2O_5+H_2O=2HPO_3$$

It reacts with hot water forming phosphoric acid.

$$P_2O_5+3H_2O=2H_3PO_4.$$

The phosphorus pentoxide has such a strong affinity for water that its principal use is as a drying agent or a dehydrating agent. In the laboratory, it is used as a drying agent in the desiccators and also used for drying gases and liquids with which it does not react. It can abstract the elements of water from many inorganic and organic compounds. Thus, it converts nitric acid into nitrogen pentoxide, sulphuric acid into sulphur trioxide.

$$2HNO_3+P_2O_5=2HPO_3+N_2O_5$$

$$H_2SO_4+P_2O_5=2HPO_3+SO_3$$

Oxy-acids of phosphorus

The principal oxyacids of phosphorus are listed in table 8.3.

Table 8.3

Name	Formula	Oxidation number	Anhydride
Hypophosphorous acid	H_3PO_2	+1	
Phosphorous acid	H_3PO_3	+3	P_2O_3
Hypophosphoric acid	$H_4P_2O_6$	+4	
Orthophosphoric acid	H_3PO_4	+5	P_2O_5
Pyrophosphoric acid	$H_4P_2O_7$	+5	P_2O_5
Metaphosphoric acid	HPO_3	+5	

The acids which are included in the syllabus are discussed here.

Phosphorous acid, H_3PO_3

Preparation. This acid is formed when phosphorus trioxide is dissolved in cold water.

$$P_2O_3+3H_2O=2H_3PO_3$$

The acid is best prepared by the action of water on phosphorus trichloride.

$$PCl_3+3H_2O=H_3PO_3+3HCl$$

The solution is concentrated by evaporation until the temperature rises to 180°C when hydrogen chloride is driven off. The concentrated solution on cooling yields crystals of phosphorous acid.

Properties. Phosphorous acid forms colourless deliquescent crystalline solids which melts at 73·6°C. When heated, it decomposes into phosphine and orthophosphoric acid.

$$4H_3PO_3=3H_3PO_4+PH_3$$

Though there are three hydrogen atoms in its molecule, H_3PO_3 is only dibasic acid of medium strength. Hence, it forms two series of salts (phosphites) : Na_2HPO_3 is normal sodium phosphite and NaH_2PO_3 is sodium hydrogen phosphite. Most of the metallic phosphites except those of Na, K and Ca are sparingly soluble in water.

On standing, the aqueous solution of phosphorous acid is gradually oxidised by atmospheric oxygen to phosphoric acid.

$$2H_3PO_3+O_2=2H_3PO_4$$

Phosphorous acid is a powerful reducing agent ; it precipitates gold and silver from their salt solutions.

$$2AuCl_3+3H_3PO_3+3H_2O=3H_3PO_4+6HCl+2Au$$

$$2AgNO_3+H_3PO_3+H_2O=H_3PO_4+2HNO_3+2Ag$$

It reduces salts of copper to metallic copper.

$$CuSO_4+H_3PO_3+H_2O=H_3PO_4+H_2SO_4+Cu$$

Mercuric chloride is reduced to mercurous chloride.

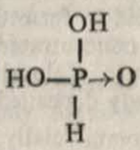
$$2HgCl_2+H_3PO_3+H_2O=H_3PO_4+2HCl+Hg_2Cl_2$$

Phosphorous acid precipitates sulphur from a solution of sulphurous acid.

$$H_2SO_3+2H_3PO_3=2H_3PO_4+H_2O+S$$

Or, $SO_2+H_2O+2H_3PO_3=2H_3PO_4+H_2O+S$

Structure. Phosphorous acid is best represented by the following structure.



$$\mathrm{HO{-}\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle H}{|}}{P}}{\rightarrow}O}$$

This structure explains its dibasic character and its reducing properties. Its reducing properties are due to the hydrogen atom directly linked to phosphorus atom. Only the two hydrogen atoms which are linked to oxygen atom ionise to give hydrogen ions. The hydrogen atom which is linked to phosphorus atom cannot ionise to give hydrogen ion. For this reason, each molecule of phosphorous acid when dissolved in water give two hydrogen ions. Hence, it acts as a dibasic acid.

The Phosphoric Acids

Three well-defined phosphoric acids are known. Depending upon temperatures, phosphorus pentoxide unites with different quantities of water to form meta-, pyro- and ortho-phosphoric acids.

$$P_2O_5 + H_2O = 2HPO_3 \text{ (metaphosphoric acid)}$$

$$P_2O_5 + 2H_2O = H_4P_2O_7 \text{ (pyrophosphoric acid)}$$

$$P_2O_5 + 3H_2O = 2H_3PO_4 \text{ (orthophosphoric acid)}$$

Phosphorus exists in the same oxidation state (+5) in all these acids. The relation between these phosphoric acids is merely the degree of hydration ; the most hydrated acid is called the ortho-acid and the least hydrated acid, the meta-acid.

Orthophosphoric Acid, H_3PO_4

The most important of the acids of phosphorus is orthophosphoric acid, H_3PO_4 commonly referred to simply as "phosphoric acid".

Preparation. It is formed when phosphorus pentoxide is dissolved in water and the solution boiled. In the laboratory, orthophosphoric acid is prepared by heating red phosphorus with concentrated nitric acid.

$$P_4 + 10HNO_3 + H_2O = 4H_3PO_4 + 5NO + 5NO_2$$

Red phosphorus is added cautiously to nitric acid (56 c.c. conc. HNO_3 + 91 c.c. water), in a litre-flask fitted with a reflux condenser. A trace of iodine which catalyses the reaction is also added to the mixture. The mixture is then heated on a water-bath until the action ceases. The resulting solution is then diluted with its own volume of water, filtered and evaporated carefully on a porcelain dish until no more fumes of oxides of nitrogen are given off, the temperature being kept below 180°C since at higher temperatures pyrophosphoric acid is formed. It is then cooled in a vacuum desiccator over fresh concentrated sulphuric acid placing the desiccator in a freezing mixture. Colourless deliquescent crystals of orthophosphoric acid are slowly deposited.

Commercial preparation. Commercially, orthophosphoric acid is prepared by digesting bone-ash or ground phosphate rock with dilute (60%) sulphuric acid for several hours. Bone-ash or phosphate rock [$Ca_3(PO_4)_2$] is decomposed by sulphuric acid into calcium sulphate and orthophosphoric acid.

$$Ca_3(PO_4)_2 + 3H_2SO_4 = 3CaSO_4 + 2H_3PO_4$$

The insoluble calcium sulphate is separated by filtration and the filtrate containing orthophosphoric acid is evaporated to a syrupy liquid.

Properties. Orthophosphoric acid is a colourless crystalline solid which melts at 40°C. It is very soluble in water. When the acid is heated, it decomposes, pyrophosphoric acid being formed at 250°C.

$$2H_3PO_4 = H_4P_2O_7 + H_2O$$

On further heating metaphosphoric acid is formed.

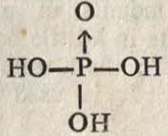
$$H_4P_2O_7 = 2HPO_3 + H_2O$$

Phosphoric acid is a moderately strong acid. It is triprotic and ionises in three stages.

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^{-1}$$
$$H_2PO_4^{-1} \rightleftharpoons H^+ + HPO_4^{-2}$$
$$HPO_4^{-2} \rightleftharpoons H^+ + PO_4^{-3}$$

Corresponding to three stages of ionisation, H_3PO_4 forms three series of salts which are known as phosphates. Examples are : NaH_2PO_4, sodium dihydrogen phosphate ; Na_2HPO_4, disodium hydrogen phosphate and Na_3PO_4, trisodium phosphate.

Structure : Orthophosphoric acid is represented by the following structure.



$$\begin{array}{c} O \\ \uparrow \\ HO—P—OH \\ | \\ OH \end{array}$$

This structure explains its tri-basic character.

The Phosphate. The salts of orthophosphoric acid are known as phosphates. Three series of salts are formed by orthophosphoric acid, viz., primary, e.g. sodium dihydrogen phosphate, NaH_2PO_4, secondary, e.g., disodium hydrogen phosphate, Na_2HPO_4 and tertiary, e.g., trisodium hydrogen phosphate, Na_3PO_4.

An aqueous solution of primary phosphate, e.g., NaH_2PO_4 is slightly acidic because it dissociates giving H^+ ion.

$$NaH_2PO_4 \rightleftharpoons Na^+ + H_2PO_4^- \; ; \; H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{-2}$$

The secondary phosphates are faintly alkaline and tertiary phosphates are strongly alkaline because they undergo hydrolysis in water.

$$Na_2HPO_4 + H_2O \rightleftharpoons NaH_2PO_4 + NaOH$$
$$Na_3PO_4 + H_2O \rightleftharpoons Na_2HPO_4 + NaOH$$

All the primary phosphates are soluble in water ; of the secondary and tertiary phosphates only those of sodium, potassium and ammonium are soluble.

The primary salt, NaH_2PO_4 and the secondary salt Na_2HPO_4 are decomposed by heat giving $NaPO_3$ and $Na_4P_2O_7$ respectively ; the tertiary salt, Na_3PO_4 is unaffected by heat.

Preparation of sodium phosphates. Disodium hydrogen phosphate, Na_2HPO_4, $12H_2O$ is prepared by adding sodium hydroxide solution to phosphoric acid to which a few drops of phenolphthalein solution have been added. The addition of NaOH is continued till the solution turns pink ; phenolphthalein changes colour at the stage Na_2HPO_4. The solution is then evaporated to crystallisation.

The primary phosphate NaH_2PO_4, H_2O is prepared by adding phosphoric acid to a solution of disodium salt until a precipitate is no longer formed when a drop of the solution is added to barium chloride solution. On evaporating the resulting solution white crystals of NaH_2PO_4, H_2O separate out.

The tertiary phosphate Na_3PO_4 is prepared by dissolving the disodium salt in excess of caustic soda solution in water. The resulting solution on crystallisation yields white crystals of tertiary phosphate, Na_3PO_4, $2H_2O$.

The microcosmic salt $NaNH_4HPO_4$, $4H_2O$ is prepared by dissolving equimolecular amounts of ammonium chloride and disodium hydrogen phosphate in a little hot water. The precipitated sodium chloride is filtered off ; the filtrate on crystallisation yields crystals of microcosmic salt. It is used in qualitative analysis for "bead" tests.

Phosphate salts are used mainly as fertilisers : NaH_2PO_4 is used as a component of "baking powder", Na_3PO_4 is used as a detergent and is used for softening hard water.

Phosphate fertilisers. The salts of phosphoric acid are of great importance in agriculture. Phosphorus is essential for plant life. Phosphorus can only be assimilated by plants when it is in the soil in a soluble form. The consumption of phosphorus by plants gradually depletes the soil and it is necessary to introduce various phosphate fertilisers into the soil in order to increase the crops.

Natural phosphate rocks, phosphorites and apatites contain phosphorus in the form of insoluble tertiary calcium phosphate $Ca_3(PO_4)_2$ which is difficult for plants to assimilate. A more soluble and suitable phosphate which is readily assimilated by plants is calcium dihydrogen phosphate, $Ca(H_2PO_4)_2$. Hence, the phosphate rocks are treated chemically in order to convert tertiary calcium phosphate, $Ca_3(PO_4)_2$ into calcium dihydrogen phosphate $Ca(H_2PO_4)_2$. Two most important phosphate fertilisers prepared from phosphate rocks are superphosphate and precipitate.

Superphosphate of lime. Superphosphate of lime is prepared by mixing finely powdered phosphate rock with enough sulphuric acid (70%) to total two molecules of H_2SO_4 for every molecule of $Ca_3(PO_4)_2$.

$$Ca_3(PO_4)_2+2H_2SO_4+4H_2O=Ca(H_2PO_4)_2+2CaSO_4, 2H_2O$$

The reaction is accompanied by the liberation of considerable amount of heat and the gases such as CO_2, SiF_4, HF and HCl which are evolved are expelled. The product is a mixture of primary phosphate $Ca(H_2PO_4)_2$ and gypsum, $CaSO_4, 2H_2O$ which are comparatively soluble in water. This mixture is called the superphosphate of lime.

Superphosphate of lime is manufactured by mixing finely ground natural phosphate rock with 70% sulphuric acid from lead chamber process in a horizontal cast-iron cylinder (mixer) fitted with revolving blades inside. The mixture passes out of the mixer in a nearly fluid state and collects in pits or dens. When the dens are half-filled, they are closed. In these pits, the reaction between sulphuric acid and tricalcium phosphate is completed. The temperature rises considerably and much gas is evolved consisting of CO_2, SiF_4, HF and HCl. The gases escape through an outlet to the absorption towers. After two or three days superphosphate formed is discharged from the pit and powdered in a crusher. They are then carefully dried in long brick-work chambers by hot air.

Sometimes, a superphosphate fertiliser containing a greater percentage of phosphorus is prepared from natural phosphate rock by first separating orthophosphoric acid by the reaction.

$$Ca_3(PO_4)_2+3H_2SO_4=3CaSO_4+2H_3PO_4$$

The precipitates of calcium sulphate are removed ; the phosphoric acid obtained is then treated with fresh batch of phosphate rock.

$$Ca_3(PO_4)_2+4H_3PO_4=3Ca(H_2PO_4)_2$$

The product is richer in phosphorus than the superphosphate of lime ; it is called the "triple superphosphate".

Precipitate. Precipitate, $CaHPO_4,H_2O$, is also a good fertiliser. Free phosphoric acid is first prepared by treating phosphate rock with sulphuric acid. The acid is then separated from the precipitate of calcium sulphate. A suspension of lime in water (milk of lime) is then added to phosphoric acid in sufficient quantity to form the secondary phosphate.

$$H_3PO_4+Ca(OH)_2=CaHPO_4, H_2O+H_2O$$

$CaHPO_4$, H_2O called precipitate separates from the liquid in crystalline form. It is carefully dried so that no water contained in crystal (water of crystallisation) is lost. It is easily assimilated by the plants.

Mixed fertilisers. The production of mixed fertilisers is acquiring great importance. The most important of these are ammonium phosphates known as "ammophoses". "Ammophos" is a mixture of $NH_4H_2PO_4$ and $(NH_4)_2\ HPO_4$ which is prepared by the direct reaction between ammonia and phosphoric acid.

A mixture of ammophos and potassium nitrate is a very useful fertiliser because it contains all "fertilising" elements, P, N and K which are essential for the growth of plants.

Tests of phosphates. Phosphates are detected by the following tests.

(i) **Cobalt nitrate test.** If a phosphate is heated in a charcoal groove with one or two drops of cobalt nitrate solution, a blue mass is formed.

(ii) On warming a nitric acid solution of orthophosphate with an excess of ammonium molybdate, a canary-yellow precipitate of ammonium phosphomolybdate is formed. Meta-phosphates, and pyrophosphates also respond to this test because they are converted into orthophosphates by heating with nitric acid.

Arsenates give the yellow precipitates on boiling.

$$Na_2HPO_4+12(NH_4)_2\ MoO_4+23HNO_3$$
$$=(NH_4)_3[PMo_{12}O_{40}]+2NaNO_3+21NH_4NO_3+12H_2O$$

EXERCISES

1. Describe the preparation of white phosphorus. How is it converted into red phosphorus ? [C. U., '57]

What is superphosphate of lime ?

2. Describe how phosphine is prepared ? What are the precautions which are usually taken during its preparation. [C. U., '57]

3. Compare phosphine with ammonia.

4. Describe the physical and chemical properties of phosphine and compare these with those of ammonia.

5. How does phosphorus occur in nature ? Outline the process of manufacturing white phosphorus and red phosphorus from phosphate rock. What are bone-black and bone-ash ? State the uses of phosphorus.

6. Write an essay on phosphate fertilisers. What are mixed fertilisers ?

7. Starting from white phosphorus, how would you prepare (a) phosphorus pentoxide, (b) phosphine, (c) red phosphorus and (d) orthophosphoric acid ?

8. Describe methods of converting phosphate rock into phosphoric acids.

Explain why a solution of NaH_2PO_4 gives a slightly acidic reaction and $Na_2H\ PO_4$ a slightly basic reaction.

9. State what happens when :

(i) white phosphorus is boiled with caustic soda solution.

(ii) red phosphorus is heated with conc. HNO_3.

(iii) white phosphorus is added to copper sulphate solution.

(iv) phosphoric acid is heated.

(v) white phosphorus is kept in contact with iodine.

(vi) a mixture of bone-ash, sand and coke is heated in an electric furnace.

(vii) phosphine gas is passed into copper sulphate solution. [H. S., '80]

(viii) a mixture of conc. HNO_3 and P_4O_{10} is heated.

(ix) phosphine gas is passed into silver nitrate solution.

(x) calcium phosphide is boiled with water.

10. Why phosphorus does not occur free in nature ? Name the important allotropes of phosphorus. [H. S., '79]

11. How does phosphorus occur in nature ? Describe the preparation of white and red phosphorus from phosphate rocks. What are bone-ash and bone-black ? Mention the uses of phosphorus.

12. How would you convert phosphate rocks into phosphoric acid ?

13. Explain the following statements :

(a) Phosphine is a stronger reducing agent than ammonia.

(b) Ammonia has basic properties.

(c) Ammonia is more basic than phosphine.

(d) Ammonia molecules can associate while phosphine molecules cannot.

(e) Phosphorous acid is a dibasic acid.

(f) The aqueous solution of Na_3PO_4 is basic.

(g) Phosphorous acid has reducing properties.

(h) The boiling point of ammonia is higher than that of phosphine.

14. How would you prepare

(a) phosphine from phosphorus and phosphorus from phosphine,

(b) phosphorium iodide from phosphine and phosphine from phosphonium iodide.

15. How would you prove that white phosphorus and red phosphorus are allotropes of the same element ?

16. Show that white phosphorus is more active than red phosphorus. [H. S., '80]

Why is white phosphorus stored in water ? [H. S., '79]

CHAPTER IX

SULPHUR AND ITS COMPOUNDS

Atomic weight, 32·066 **Atomic number, 16**

Electron configuration, $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$

Sulphur was one of the few elements which was known to the ancients. It is mentioned in the Bible and in Homer. Alchemists regarded sulphur as the "principle of fire". In 1777, Lavoisier considered it to be an element. The name sulphur is derived from the Sanskrit "sulveri".

Sulphur occurs in nature both in free state as native sulphur and in the combined state. Deposits of free sulphur are found in the volcanic regions of Italy, Sicily and Japan and in Louisiana and Texas, U.S.A. In combination, sulphur is more widely distributed as sulphides and sulphate. Among the sulphides are *iron pyrites*, FeS_2 ; *galena*, PbS ; *cinnabar*, HgS ; and *zinc blende* ZnS. Among the sulphate minerals are *epsom salts*, $MgSO_4$, $7H_2O$; *gypsum*, $CaSO_4$, $2H_2O$ and *barytes*, $BaSO_4$.

Sulphur is an essential constituent in living matter. It occurs in animal and vegetable products such as proteins, eggs, many oils, onions, garlic, mustard, hair, etc. The total sulphur content in the earth's crust is around 0·10 per cent.

The extraction of sulphur. (i) **Sicilian method.** The crude sulphur dug up in Sicily consists of rocks such as clay, gypsum, limestone, etc., mixed with about 20 per cent of free sulphur. Sulphur is separated from the rocks by heating the ore and allowing the molten sulphur to flow away from the rocks. Sulphur is melted by the heat evolved due to the combustion of the sulphur itself or of some other fuel.

Fig. 9.1 is a diagram of a sulphur kiln which is a roofless chamber built of stone. Its floor slopes down towards the front wall. The front wall is provided at its bottom with an outlet which is plugged up with a thin partition of plaster of paris. The kiln is filled with the lumps of ore, leaving air channels between the lumps and forming a cone at the top. The ore is kindled at the top with bunches of straw or brushwood and the heat evolved due to the burning of part of sulphur serves to melt the rest. The molten sulphur seeps down and flows out of the kiln.

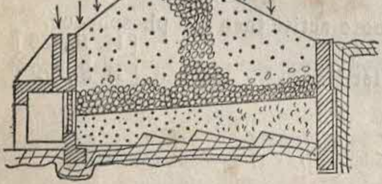


Fig. 9.1

The heat produced by burning sulphur can be utilised more fully by using the Gill's kiln which consists of a number of communicating chambers. The hot gases produced by burning sulphur in one chamber pass into the adjoining chamber and melt the crude sulphur there. Consequently, sulphur is saved and heat is economised.

The crude sulphur contains about 5% of the rocky impurity. It is purified by distillation. The distillation apparatus is shown in fig. 9.2. Crude sulphur is melted in an iron pot (A). The molten sulphur then flows into the iron retort (B) where it is heated to boiling. The sulphur vapours then pass into a large brick-work chamber (C). At first when the chamber is still cold, sulphur condenses on the cold walls as a light yellow powder of flower of sulphur. After the chamber has been heated above 120°C, sulphur condenses into a liquid which is drawn off through the opening (D) and tapped off into wooden moulds where it solidifies into rods. Sulphur obtained in this way is known as roll sulphur or *brimstone*.

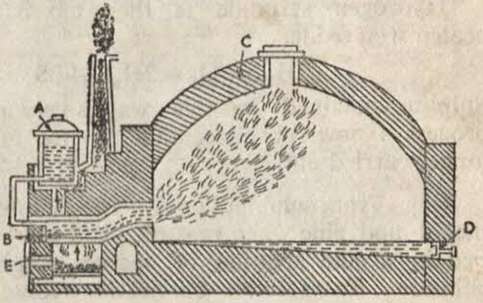


Fig. 9.2

(ii) **The Frasch process.** About 80% of the world's sulphur are now obtained from the sulphur deposits in Louisiana and Texas. These deposits occur at depths of about 900 feet under strata of sand, clay and rock. Their extraction by ordinary mining is impossible owing to the quicksands and to the presence of poisonous gases, hydrogen sulphide and sulphur dioxide. In the Frasch process, a boring is made through the overlying materials until the beds of sulphur are reached and four concentric pipes are sunk. Water superheated under pressure to about 170°C is forced downward through the two outer pipes. This melts the sulphur which collects in a pool at the bottom of the well. Hot compressed air is then forced to the bottom through the innermost pipe when froths of air, sulphur and water are formed. The froths are forced up to the surface through the remaining pipes. The mixture is run into wooden vats where the sulphur solidifies. Its purity is 99·5 per cent.

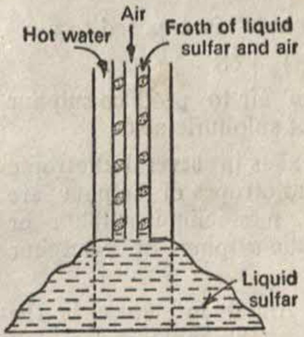


Fig. 9.3

(iii) **Extraction of sulphur from alkali waste.** Alkali waste of Leblanc carbonate process contains insoluble calcium sulphide, CaS. The waste is mixed with water in large iron vessels and limekiln gas (CO_2 and N_2) is passed through the mixture, when hydrogen sulphide is evolved.

$$CaS+CO_2+H_2O=CaCO_3+H_2S$$

Hydrogen sulphide is then mixed with air and passed over heated iron oxide.

$$2H_2S+O_2=2H_2O+2S$$

Sulphur obtained in this way is very pure. Since the Leblanc process is now obsolete, this process of extracting sulphur is no longer carried out.

(iv) **From sulphide ores.** The sulphide ores of copper, lead, nickel and zinc when roasted, yield sulphur dioxide which is absorbed in a cold solution of sodium sulphite containing aluminium chloride. The solution on heating evolve sulphur dioxide which is then passed over white hot-coke when SO_2 is reduced to sulphur.

$$Na_2SO_3+SO_2+H_2O=2NaHSO_3$$

$$SO_2+C=CO_2+S$$

(v) **From coal.** Coal contains pyrites FeS_2. During distillation in the manufacture of coal gas, about half the sulphur comes off as hydrogen sulphide and carbon disulphide. Hydrogen sulphide is then passed into purifiers which contains hydrated ferric oxide. Ferric oxide reacts with H_2S forming ferric sulphide.

$$2Fe(OH)_3+3H_2S=Fe_2S_3+6H_2O$$

Sulphur is separated out when the "spent oxide" is exposed to air.

$$2Fe_2S_3+3O_2+6H_2O=4Fe(OH)_3+6S$$

Usually the "spent oxide" is burnt in air to produce sulphur dioxide which is used in the manufacture of sulphuric acid.

Allotropic forms of sulphur. Sulphur exists in several allotropic modifications. Two common crystalline allotropes of sulphur are (i) rhombic sulphur or α-sulphur and (ii) monoclinic sulphur or β-sulphur. Amorphous forms such as plastic sulphur or γ-sulphur are also known.

(i) **Rhombic or α-sulphur.** Sulphur is found in nature in the form of large yellow crystals which belong to rhombic system. It may be prepared in the laboratory by dissolving pure native sulphur in carbon disulphide and evaporating the solution slowly when transparent yellow crystals of rhombic sulphur crystallise from the solution. It has a density of 2·07 gram/ml at 20°C. It melts at 112·8°C and boils at 444·6°C. It is insoluble in water but soluble in carbon disulphide, carbon tetrachloride and similar other solvents. It is stable below 95·5°C under normal atmospheric pressure. Between 95·5°C and its melting point it undergoes slow transformation into the monoclinic variety.

(ii) **Monoclinic sulphur or β-sulphur.** This form is obtained by melting roll sulphur in a crucible and allowing it to cool slowly. When the liquid has partly solidified, two holes are made into the crusts on the surface and the portion still in the liquid form is poured off. The sides of the vessel will then be found to be covered on the inside with a mass of long, dark-yellow, needle shaped crystals of monoclinic sulphur.

It has a density of 1·96 gram/ml. at 20°C. It melts at 118·9°C. It is soluble in carbon disulphide. Below 95·5°C, monoclinic sulphur changes back into the rhombic sulphur. The change of the rhombic sulphur to the monoclinic sulphur is endothermic.

$$S_{\text{rhombic}} + 70 \text{ cal} \rightleftharpoons S_{\text{monoclinic}}$$

$$\text{or,}\quad S\alpha + 70 \text{ cal} \rightleftharpoons S\beta$$

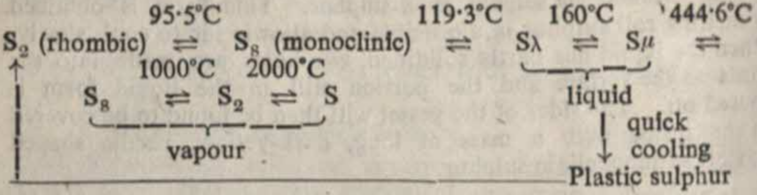
Above 95·5°C, the stable form is monoclinic sulphur and below 95·5°C, the stable form is the rhombic sulphur. This temperature at which both forms are in equilibrium is called the transition temperature of sulphur. Both rhombic and monoclinic sulphur have the molecular formula, S_8.

(iii) **Plastic or γ-sulphur.** If molten sulphur heated to near its boiling point is poured in a thin stream into cold water, it turns into a very viscous, transparent elastic mass. The mass is so viscous that it can be drawn out into threads. This modification is called plastic or γ-sulphur. It has density of 1·92 gram/ml. It is insoluble in carbon disulphide. On standing for few hours, it becomes first brittle, then acquires a yellow colour and undergoes gradual transformation into rhombic sulphur.

Liquid sulphur. If sulphur is heated slowly, very interesting changes occur. At 112·8°C, it melts into a mobile, straw coloured liquid. The viscocity of this liquid is low. On further heating, it gradually darkens in colour and becomes more viscous and at about 230°C it becomes so thick that the vessel can be turned upside down without pouring out the sulphur. The straw yellow mobile liquid is called λ-sulphur ($S\lambda$) and the dark brown viscous liquid is called the μ-sulphur ($S\mu$). Above 230°C the viscocity of the liquid decreases and the mass becomes more and more mobile as the temperature rises and finally at 444·6°C, the liquid begins to boil giving off an orange-yellow vapour. When the liquid is allowed to cool slowly, the same phenomena are repeated in the reverse order.

Just above the boiling point, sulphur vapour consists chiefly of S_2 molecules.

At higher temperatures, it gradually dissociates forming S_6 and S_2 molecules. At 2000°C, sulphur vapour consists of simple monatomic molecules. The series of changes that sulphur undergoes with change in temperature may be represented as follows :



Milk of sulphur. This is prepared by boiling powdered roll sulphur with milk of lime. The solution is filtered and the reddish yellow filtrate which contains calcium pentasulphide and calcium thiosulphate is acidified with dilute hydrochloric acid, when white amorphous precipitate of milk of sulphur is deposited.

$$3Ca(OH)_2+12S=2CaS_5+CaS_2O_3+3H_2O$$

$$2CaS_5+CaS_2O_3+6HCl=3CaCl_2+3H_2O+12S$$

Milk of sulphur is soluble in cabon disulphide. It is used medicinally.

Colloidal sulphur. It may be prepared by various methods. When alcoholic solution of sulphur is poured into water colloidal sulphur is formed. It can also be prepared by acidifying sodium thiosulphate solution with sulphuric acid.

$$Na_2S_2O_3+H_2SO_4=Na_2SO_4+H_2O+SO_2+S$$

It is also formed when hydrogen sulphide is passed into sulphur dioxide solution.

$$SO_2+2H_2S=2H_2O+3S$$

Sulphur is precipitated from the solution by adding sodium chloride which coagulates colloidal sulphur. It is used in medicine.

Properties of sulphur. (A) **Physical properties :** Pure native sulphur is a yellow crystalline substance. It is a poor conductor of heat and electricity. It is insoluble in water but soluble in carbon di-sulphide. It boils at 444·6°C under 760 mm. pressure ; this temperature is sufficiently constant to be used as a fixed point in thermometry.

(B) **Chemical properties :** Sulphur has six electrons in its outermost energy level and hence will combine with any elements which can furnish two electrons or an interest in two electrons. Consequently, sulphur is a reactive element and combines with most of the elements, especially when heated.

Sulphur combines directly with all of the non-metals except the inert gases, iodine and nitrogen.

(i) **Reaction with non-metals.** It burns in air or oxygen with a blue flame to form sulphur dioxide, SO_2 and a little sulphur trioxide, SO_3.

$$S+O_2=SO_2$$

When heated sulphur combines with hydrogen forming hydrogen sulphide, the reaction being slow and reversible.

$$H_2+S \rightleftharpoons H_2S$$

Sulphur reacts with halogen forming a variety of halides. Thus, it burns in fluorine spontaneously yielding sulphur hexafluoride.

$$S+3F_2=SF_6$$

Sulphur monochloride is formed when dry chlorine is passed into boiling sulphur.

$$2S+Cl_2=S_2Cl_2$$

Sulphur monobromide is formed by heating bromine with sulphur.

$$2S+Br_2=S_2Br_2$$

When sulphur vapour is passed over a bed of glowing coke, carbon disulphide is formed.

$$2S+C=CS_2$$

Sulphur reacts explosively with yellow phosphorus when heated forming phosphorus sulphides. It reacts with red phosphorus more slowly.

(ii) **Reaction with metals.** Sulphur is a typical non-metal and combines with all metals except gold and those of the platinum family to produce the sulphides. In some cases, the reaction takes place with the evolution of heat. When sulphur and mercury are rubbed in a mortar, mercuric sulphide is formed.

$$Hg+S=HgS$$

When a thin strip of copper is inserted into the vapours of sulphur, the metal burns brilliantly forming copper sulphide.

$$Cu+S=CuS$$

Sulphur reacts with iron when heated forming ferrous sulphide.

$$Fe+S=FeS$$

Alkali metal sulphides are formed when alkali metals are heated with sulphur.

$$2Na+S=Na_2S$$

(iii) **Reaction with compounds.** Sulphur is oxidised by hot concentrated sulphuric acid to sulphur dioxide.

$$S+2H_2SO_4=3SO_2+2H_2O$$

Hot concentrated nitric acid oxidises it to sulphuric acid.

$$S+6HNO_3=H_2SO_4+6NO_2+2H_2O$$

Sulphur dissolves in alkalis to form primarily a mixture of sulphide and sulphite.

$$3S + 6KOH = 2K_2S + K_2SO_3 + 3H_2O$$

The sulphide and sulphite formed in this reaction may unite with further quantity of sulphur to form respectively polysulphides such as K_2S_2, K_2S_4 and thiosulphates, $K_2S_2O_3$. Therefore, these compounds are present in the solution of sulphur in alkali. When sulphur is boiled with a suspension of slaked lime, calcium pentasulphide and calcium thiosulphate are formed.

$$12S + 3Ca(OH)_2 = CaS_2O_3 + 2CaS_5 + 3H_2O$$

When potassium carbonate is fused with sulphur, a liver-brown mass containing a mixture of polysulphides and thiosulphate is obtained.

$$6S + 3K_2CO_3 = K_2S_2O_3 + 2K_2S_2 + 3CO_2$$

This mixture is used in medicine under the name of *liver of sulphur*. Sulphur does not react with cold water, but a little sulphur dioxide and hydrogen sulphide are formed if steam is passed through boiling sulphur.

$$3S + 2H_2O = 2H_2S + SO_2$$

Uses of sulphur. (i) Large quantities of sulphur are burnt to sulphur dioxide which, in turn, is used for the manufacture of sulphuric acid and for the preparation of bisulphite for the paper and pulp industry.

(ii) Large quantities of sulphur are used in the vulcanization of rubber—a process in which rubber is mixed with sulphur and heated to a definite temperature when it acquires its valuable properties, namely, resilience, elasticity, etc. Rubber containing a large quantities of sulphur is known as ebonite which is an excellent electrical insulator.

(iii) Sulphur is largely used in the manufacture of variety of reagents such as carbon disulphide and in the manufacture of pigments such as vermilion (mercuric sulphide) and ultramarine. It is also used in the manufacture of matches, enamel and black gunpowder which is a mixture of sulphur, carbon and potassium nitrate.

(iv) A type of cement is made from sand and molten sulphur. *Petrasul* which is a synthetic stone is made from asbestos fibres, cement and sulphur. *Lavasul* vessels which are used for storing corrosive liquids are prepared from powdered coke and sulphur.

(v) Large quantities of flowers of sulphur are used to destroy certain orchard pests. It is used in medicine for the treatment of skin diseases.

Hydrogen sulphide or Sulphuretted hydrogen, H_2S.

Hydrogen sulphide was known by its smell to the alchemists of the middle ages. In 1777, K. W. Scheele first investigated the compound systematically and proved that it is a compound of hydrogen and sulphur.

Hydrogen sulphide occurs in volcanic gases and in several mineral waters. Natural gas also frequently contains hydrogen sulphide. It is always formed when animal and plant matter containing sulphur decompose in a limited supply of air. The gas contributes to the smell of rotten eggs.

Preparation (i) By the direct union of hydrogen and sulphur. At ordinary temperature, hydrogen and sulphur do not combine, but with the increase of temperature, the combination takes place and becomes almost complete at 350°C. The reaction takes place very slowly. The reaction can be brought about more conveniently by boiling sulphur in an atmosphere of hydrogen and passing the resulting mixture over finely divided nickel at 450°C when almost complete combination takes place. Hydrogen sulphide formed is condensed out by cooling with solid carbon dioxide. The gas is then freed from sulphur by subsequent evaporation and dried with phosphorus pentoxide. It is then collected over mercury. Hydrogen sulphide thus obtained is very pure.

$$H_2 + S \rightleftharpoons H_2S + 2{\cdot}73 \text{ kcal}$$

The reaction is exothermic and hence the reverse reaction becomes more and more important when the temperature is increased above 500°C.

(ii) By the action of dilute acids on metal sulphides. Laboratory method. In the laboratory, hydrogen sulphide is most readily prepared by treating metal sulphides with dilute acids. For ordinary purposes ferrous sulphide and dilute hydrochloric acid or sulphuric acid are usually employed.

$$FeS + 2HCl = FeCl_2 + H_2S$$
$$FeS + H_2SO_4 = FeSO_4 + H_2S$$

Few pieces of ferrous sulphide are taken in a Woulf's bottle fitted with a thistle funnel and a delivery tube. Dilute hydrochloric acid are poured down the thistle funnel in sufficient quantity so that the end of the thistle funnel dips below the surface of the acid. Hydrochloric acid at once reacts with ferrous sulphide evolving hydrogen sulphide. The gas is collected by the upward displacement of air or over hot water.

Purification. The gas thus obtained is not pure. It contains, in addition to acid sprays, hydrogen which is formed by the action of free iron on acids. Iron is always present as impurities in ferrous sulphide which is made by heating iron and sulphur together. The gas may also contain traces of hydrocarbon derived from the action of the acids on the impurities in the iron.

Acid spray is removed by passing the gas through a saturated solution of sodium hydrogen sulphide.

$$NaHS + HCl = NaCl + H_2S$$

The gas is then passed over phosphorus pentoxide when moisture is removed. The gas still contains hydrogen which is removed by solidifying the gas with liquid air. Hydrogen is not condensed under these conditions and so can be pumped off. The solid is then allowed to warm up slowly and the first portion of the gas is allowed to escape. Later portion of the gas is very pure hydrogen sulphide.

Hydrogen sulphide free from hydrogen may be prepared by heating antimony sulphide with concentrated hydrochloric acid.

$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S$$

The gas is then passed through water contained in a wash-bottle to remove hydrogen chloride and then over phosphorus pentoxide to remove moisture. It is then collected by the upward displacement of air. The gas cannot be dried over concentrated sulphuric acid which oxidises the gas to sulphur.

$$H_2SO_4 + H_2S = 2H_2O + SO_2 + S$$

The gas cannot be dried with anhydrous calcium chloride because it reacts with calcium chloride to form calcium sulphide and hydrochloric acid.

$$CaCl_2 + H_2S = CaS + 2HCl$$

If hydrogen sulphide is not dry, pure and free from oxygen, it reacts with mercury. Hence, impure hydrogen sulphide cannot be collected over mercury.

(iii) Hydrogen sulphide is conveniently prepared by heating a mixture of sulphur and paraffin (2 : 1 by weight) with crushed asbestos to about 300°C. The reaction ceases on cooling but by reheating it can be started again.

Properties. (A) **Physical properties.** Hydrogen sulphide is a colourless gas having the smell of rotten egg. Actually, rotten eggs owe much of their unpleasant smell to hydrogen sulphide which is formed by the anaerobic decomposition of proteins containing sulphur. The gas is very poisonous ; prolonged inhalation of the gas causes serious poisoning. It is soluble in water and the solution is called hydrogen sulphide water. A solution of hydrogen sulphide in water turns blue litmus red and in general possesses acidic properties. This acid is sometimes called hydrosulphuric acid. Hydrogen sulphide can be expelled completely from its aqueous solution by boiling. It condenses to a colourless liquid which boils at $-60{\cdot}75$°C. The liquid hydrogen sulphide is a non-conductor of electricity. The gas is heavier than air and hence can be collected by the upward displacement of air.

(B) **Chemical properties** : (i) **Stability to heat.** Hydrogen sulphide is not very stable, because its molar heat of formation is only 4·8 kcal. When heated it decomposes into its elements and above 1700°C, it is dissociated completely.

$$H_2S = H_2 + S$$

Hydrogen sulphide is less stable than hydrogen chloride but more stable than phosphine.

(ii) In excess of air, or oxygen, hydrogen sulphide burns with a bluish flame to form sulphur dioxide and water.

$$2H_2S + 3O_2 = 2H_2O + 2SO_2$$

but in a limited supply of air or oxygen the product is sulphur and water because hydrogen has the greater affinity for oxygen.

$$2H_2S + O_2 = 2H_2O + 2S$$

(iii) **Reaction with metals.** At high temperatures, metals whose sulphides are stable react with hydrogen sulphide.

$$Cu + H_2S = CuS + H_2\ ;\ Sn + H_2S = SnS + H_2\ ;\ Pb + H_2S = PbS + H_2$$

The tarnishing of silver in air containing a trace of hydrogen sulphide is due to the formation of a black sulphide film.

$$4Ag + 2H_2S + O_2 = 2Ag_2S + 2H_2O$$

(iv) **Reducing property.** (a) Halogens are reduced by hydrogen sulphide to hydrohalic acids.

$$H_2S + Cl_2 = S + 2HCl$$

$$H_2S + Br_2 = S + 2HBr\ ;\quad H_2S + I_2 = S + 2HI.$$

A solution of hydrogen sulphide reacts slowly with large excess of chlorine-water forming sulphuric acid.

$$H_2S + 4H_2O + 4Cl_2 = H_2SO_4 + 8HCl$$

(b) In presence of moisture, hydrogen sulphide reduces sulphur dioxide to sulphur.

$$2H_2S + SO_2 = 3S + 2H_2O$$

The sulphur-deposits in volcanic regions are thought to be due to the reaction of the gases SO_2 and H_2S both of which are present in volcanic gases.

Hydrogen sulphide acts as a reducing agent in aqueous or alcoholic solution. It reduces a wide variety of compounds ; in most cases it is oxidised to free sulphur. Thus it reduces ferric-chloride to ferrous chloride.

$$2FeCl_3 + H_2S = 2FeCl_2 + 2HCl + S$$

Nitric acid is reduced to nitrogen dioxide.

$$2HNO_3 + H_2S = 2NO_2 + 2H_2O + S$$

Hydrogen sulphide reduces potassium permanganate ; thus when it is passed through a pink solution of potassium permanganate acidified with dilute sulphuric acid, the pink colour disappears and sulphur is precipitated.

$$2KMnO_4+3H_2SO_4+5H_2S=K_2SO_4+2MnSO_4+8H_2O+5S$$

When hydrogen sulphide is passed through a solution of potassium dichromate acidified with dilute sulphuric acid, the orange colour of the solution is converted into green colour owing to the reduction of potassium dichromate and sulphur is deposited.

$$K_2Cr_2O_7+4H_2SO_4+3H_2S=K_2SO_4+Cr_2(SO_4)_3+7H_2O+3S$$

Hydrogen sulphide reduces sulphuric acid to sulphur dioxide.

$$H_2SO_4+H_2S=2H_2O+SO_2+S$$

(v) **Acid properties.** The solution of H_2S in water behaves as an extremely weak acid called hydrosulphuric acid. It is a diprotic acid and ionises in two stages.

$$H_2S \rightleftharpoons H^+ + HS^-$$
$$HS^- \rightleftharpoons H^+ + S^{-2}$$

Hence, it forms two types of salts, hydrogen salts and normal salts, e.g., NaHS and Na_2S. Thus it reacts with sodium hydroxide to form sodium hydrogen sulphide and sodium sulphide.

$$NaOH+H_2S=NaHS+H_2O$$
$$NaHS+NaOH=Na_2S+H_2O$$

(vi) Aqueous hydrogen sulphide precipitates the sulphides of some metals from acid solution of their salts, e.g., copper, lead, cadmium, mercury, arsenic, etc.,

$$CuSO_4+H_2S=CuS+H_2SO_4$$
$$CdCl_2+H_2S=CdS+2HCl$$
$$Pb(NO_3)_2+H_2S=PbS+2HNO_3$$

Sulphides of many metals are precipitated by H_2S from alkali solution of their salts, e.g., zinc, cobalt, nickel, etc.

$$ZnSO_4+H_2S=ZnS+H_2SO_4$$
$$CoSO_4+H_2S=CoS+H_2SO_4$$

Thus, it is possible to precipitate selectively the sulphides of the metals from solutions of their salts. This selective precipitation of metal sulphides by H_2S is the basis of the classical scheme of qualitative analysis.

(vii) When hydrogen sulphide is passed through a suspension of magnesium oxide in water, a solution of magnesium hydrosulphide is obtained. On heating this solution at 60°C, pure H_2S is evolved.

$$MgO+2H_2S=Mg(HS)_2+H_2O$$

Structure of hydrogen sulphide. The molecule of hydrogen sulphide is covalent ; its electronic structure is $\mathrm{H}{}^{\times}_{\bullet}\underset{\mathrm{H}}{\underset{\cdot\times}{\overset{\cdot\cdot}{\mathrm{S}}}}\!:$ The H-S-H angle is 92°. It is analogous to that of its oxygen counterpart water.

Uses of hydrogen sulphide. It is used as a reagent for separation and identification of the metals in qualitative analysis.

Absorbent. The gas is absorbed by (i) lead nitrate solution and (ii) potassium or sodium hydroxide solution.

Sulphides. Neutral salts of hydrosulphuric acid (containing the S^{--} ion) are known as sulphides while the acid salts (containing the HS^- ion) are known as hydrosulphides. The sulphides of alkali and alkaline-earth metals are prepared on a commercial scale by heating sulphates with powdered charcoal ; thus sodium sulphate when heated with charcoal yields sodium sulphide.

$$Na_2SO_4+4C=Na_2S+4CO$$

Sulphides of some metals can be obtained by the direct union of the metals with sulphur. Thus, when a mixture of iron filings and sulphur is heated, iron sulphide is formed.

$$Fe+S=FeS$$

The sulphides of the metals which are insoluble in water are prepared by the action of hydrogen sulphide on aqueous solutions of their salts. For instance, if hydrogen sulphide is passed through a solution of any copper salt, a black precipitate of cupric sulphide immediately appears.

$$CuSO_4+H_2S=CuS+H_2SO_4$$

or in the ionic form, $Cu^{++}+H_2S=CuS+2H^+$

The precipitate is also insoluble in dilute acid. If the precipitate were soluble in dilute acids, it would not form at all because acid is formed in the reaction. Ferrous sulphide which is soluble in dilute acids can be conveniently prepared by treating a solution of ferrous salt with a solution of sodium sulphide instead of H_2S, since no acid will be formed during the reaction and ferrous sulphide is thrown down directly as a black precipitate.

$$FeSO_4+Na_2S=FeS+Na_2SO_4$$

Properties. Metallic sulphides are non-volatile solids. The sulphides of sodium, potassium and ammonium are hydrolysed in water to produce an alkaline solution.

$$Na_2S+H_2O\rightleftharpoons NaHS+NaOH$$

The sulphides of aluminium, chromium and magnesium hydrolyse almost completely when dissolved in water ; thus if ammonium sulphide solution is added to the solution of aluminium salt, aluminium hydroxide is precipitated due to the hydrolysis of aluminium sulphide formed.

$$2AlCl_3+3(NH_4)_2S=6NH_4Cl+Al_2S_3$$

$$Al_2S_3+6H_2O=2Al(OH)_3+3H_2S$$

The sulphides of calcium, barium and strontium react very slowly with water forming hydroxides and hydrosulphides of the corresponding metal since they are slightly soluble in water.

$$2CaS+2H_2O=Ca(HS)_2+Ca(OH)_2$$

When the sulphides of some metals are roasted in air, sulphur dioxide and metallic oxides are formed, e.g.,

$$4FeS_2+11O_2=2Fe_2O_3+8SO_2$$

Detection of hydrogen sulphide and sulphides. Hydrogen sulphide is detected by the following tests :

(i) It gives the smell of rotten eggs.

(ii) When a filter paper soaked with a solution of lead acetate is exposed to the gas, a lustrous brownish to black film of lead sulphide is formed on the paper.

$$Pb(CH_3COO)_2+H_2S=PbS+2CH_3COOH$$

(iii) If a drop of aqueous solution of a sulphide is placed on a bright silver surface, characteristic dark stains appear on the surface.

(iv) If the solution of a sulphide is treated with alkaline sodium nitroprusside solution, purple colouration is produced.

$$Na_2S+Na_2[FeNO(CN)_5]=Na_4[FeNOS(CN)_5]$$

(v) The presence of sulphide in insoluble sulphides is detected by heating the sulphide with granular zinc and strong hydrochloric acid. Nascent hydrogen produced reduces the sulphide with the production of hydrogen sulphide which is detected by its action on lead acetate paper.

$$CuS+2HCl+Zn=ZnCl_2+Cu+H_2S$$

Oxides of Sulphur

As many as six different oxides of sulphur are known ; only two of these, the sulphur dioxide, SO_2 and sulphur trioxide, SO_3 are of importance.

Sulphur dioxide, SO_2

In 1770, J. Priestley first obtained the gaseous sulphur dioxide by the action of hot concentrated sulphuric acid on mercury and collected the gas over mercury. He called it "vitriolic acid air". The composition of the gas was determined by Lavoisier in 1777.

Sulphur dioxide occurs in volcanic gases and in the springs of volcanic districts. Traces of the gas are present in the atmosphere, being derived from the roasting of sulphide ores and combustion of iron pyrites contained in coal and from many industrial operations.

Preparation. Sulphur dioxide can be prepared by the following processes.

(i) **By the burning of sulphur.** When ignited in air, sulphur burns with a blue flame, forming sulphur dioxide together with a little sulphur trioxide.

$$S+O_2=SO_2$$

The products of combustion are then passed up a tower down which a stream of cold water flows. Sulphur dioxide dissolves in water. On heating the solution, the gas is expelled from the solution. It is then dried by refrigeration and by exposure to sulphuric acid. Finally, it is liquefied by compression. The liquid SO_2 is stored in steel cylinders.

(ii) **By the burning of pyrite.** Sulphur dioxide is prepared on a large scale by burning iron pyrites in air.

$$4FeS_2+11O_2=2Fe_2O_3+8SO_2$$

The crude gas from the pyrite burners contains impurities such as arsenious oxide, As_2O_3, sulphur trioxide and dust particles. The gas is purified by passing it through settling chambers, coke filters and coke towers down which is flowing sulphuric acid.

(iii) **By the roasting of sulphide ores.** Sulphur dioxide can also be prepared by roasting ores containing sulphur such as zinc blende, copper pyrites, etc.

$$2ZnS+3O_2=2ZnO+2SO_2$$

Sulphur dioxide by this process is often immediately employed in the manufacture of sulphuric acid.

The foregoing methods are used in the preparation of sulphur dioxide on a large scale and hence are not suitable for the preparation of small quantities of sulphur dioxide for use in laboratory. In the laboratory preparation, the following methods are commonly employed.

(iv) (a) **By the reduction of sulphuric acid by an oxidisable element. Laboratory preparation.** In the laboratory, sulphur dioxide is usually prepared by reducing concentrated sulphuric acid by oxidisable elements the commonest of which are copper and carbon.

$$2H_2SO_4+Cu=CuSO_4+SO_2+2H_2O$$

$$2H_2SO_4+C=CO_2+2SO_2+2H_2O$$

Copper turnings are taken in a flask which is fitted with a thistle funnel and a delivery tube. Concentrated sulphuric acid is added through the thistle funnel in sufficient quantity so that the end of the thistle funnel dips under the surface of the acid. The flask is then heated on wire gauze and the mixture becomes dark and sulphur dioxide is evolved with effervescence. The gas is then collected by the upward displacement of air. It may be dried by passing it through a wash-bottle containing concentrated sulphuric acid and collected over mercury. It can also be dried by anhydrous calcium chloride or phosphorus pentoxide.

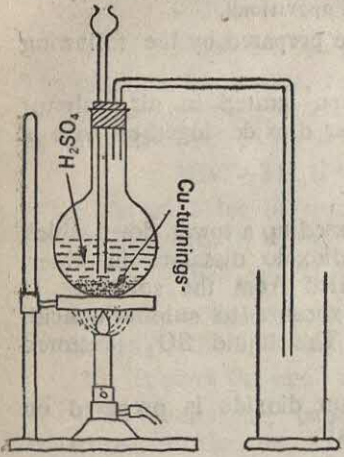


Fig. 9.4

N.B. : Copper sulphate, $CuSO_4$, $5H_2O$ can be recovered from the residue left in the flask. After cooling, the residue is warmed with water and the solution is filtered. The filtrate is evaporated and set aside. Copper sulphate separates out of the solution in the form of deep-blue crystals.

(b) By the action of acids on sulphites or bi-sulphites. In the laboratory, sulphur dioxide can also be prepared by adding an acid to a cocentrated solution of sulphites or bisulphites. Thus, when concentrated sulphuric acid is added dropwise to a concentrated solution of sodium bisulphite, sulphur dioxide is evolved.

$$NaHSO_3 + H_2SO_4 = NaHSO_4 + SO_2 + H_2O$$
$$Na_2SO_3 + 2HCl = 2NaCl + SO_2 + H_2O$$
$$NaHSO_3 + HCl = NaCl + SO_2 + H_2O$$

Properties. (A) **Physical properties.** Sulphur dioxide is a colourless gas with a pungent odour of burning sulphur. It is $2\frac{1}{2}$ times as heavy as air. It condenses quite readily to a colourless liquid ; at normal pressure it liquefies at $-10{\cdot}02°C$. The liquid freezes at $-74{\cdot}46°C$ to a snowy solid. Rapid evaporation of some of the liquid will cause the remainder to freeze.

The gas is very soluble in water. The solution contains the unstable weak acid, H_2SO_3 which is formed by the reaction between part of sulphur dioxide dissolved and water.

$$SO_2 + H_2O \rightleftharpoons H_2SO_3$$

All the sulphur dioxide can be completely expelled from the solution by boiling.

(B) Chemical properties. (i) **Stability to heat.** Sulphur dioxide is stable to heat. The gas is appreciably dissociated to sulphur trioxide and sulphur at 1200°C.

$$3SO_2 \rightleftharpoons S + 2SO_3$$

(ii) Sulphur dioxide is incombustible and it does not support the combustion of hydrogen. At high temperatures and in the presence of suitable catalyst such as platinum sulphur dioxide combines with oxygen forming sulphur trioxide, the reaction being reversible.

$$2SO_2+O_2 \rightleftharpoons 2SO_3$$

This attachment of oxygen atom to sulphur dioxide molecule to form sulphur trioxide molecule is possible due to the presence of unused pair of electrons on sulphur atom of SO_2 molecule (see molecular structure of SO_2).

The anhydrous sulphur dioxide reacts with anhydrous chlorine, bromine and fluorine forming sulphuryl chloride, sulphuryl bromide, and sulphuryl fluoride respectively. The reaction is catalysed by camphor and charcoal.

$$SO_2+Cl_2=SO_2Cl_2 \; ; \; SO_2+Br_2=SO_2Br_2 \; ; \; SO_2+F_2=SO_2F_2$$

(iii) **Reaction with metals.** Some metals burn in sulphur dioxide by abstracting its oxygen. For example, finely divided tin, and iron burn in the gas when heated forming oxides and sulphides. Zinc reacts with sulphur dioxide forming zinc hyposulphite.

$$Zn+2SO_2=ZnS_2O_4$$

Heated potassium burns in it forming sulphite and thiosulphate.

$$4K+3SO_2=K_2SO_3+K_2S_2O_3$$

(iv) **Acid properties.** The aqueous solution of sulphur dioxide acts as a weak dibasic acid. If sulphur dioxide is passed through a solution of sodium hydroxide till the solution is saturated, sodium bisulphite is formed.

$$NaOH+SO_2=NaHSO_3$$

With excess of sodium hydroxide, it forms normal salt.

$$NaOH+NaHSO_3=Na_2SO_3+H_2O$$

Sodium metabisulphite is made by evaporating a solution of sodium-bisulphite

$$2NaHSO_3=Na_2S_2O_5+H_2O$$

This is used in photography as a developer.

It reacts with sodium carbonate in a similar manner; thus if the solution of sodium carbonate is saturated with sulphur dioxide, sodium bisulphite is formed and if sodium carbonate is in excess sodium sulphate results.

$$Na_2CO_3+H_2O+2SO_2=2NaHSO_3+CO_2$$

$$2NaHSO_3+Na_2CO_3=2Na_2SO_3+CO_2+H_2O$$

When sulphur dioxide is passed through lime water, lime water turns milky because of the formation of insoluble calcium sulphite.

If excess of the gas is passed through the solution, calcium sulphite dissolves forming soluble calcium bisulphite and hence milkiness of the solution disappears.

$$Ca(OH)_2+SO_2=CaSO_3+H_2O$$
$$CaSO_3+H_2O+SO_2=Ca(HSO_3)_2$$

(v) **Reducing properties.** Aqueous solution of sulphur dioxide is a good reducing agent. It reduces halogens to the halogen acids. Thus when sulphur dioxide is passed through chlorine water, bromine water and through suspension of iodine in water, hydrochloric acid, hydrobromic acid and hydriodic acid are respectively formed.

$$SO_2+Cl_2+2H_2O=2HCl+H_2SO_4$$
$$SO_2+Br_2+2H_2O=2HBr+H_2SO_4$$
$$SO_2+I_2+2H_2O=2HI+H_2SO_4$$

It is oxidised to sulphuric acid by atmospheric oxygen.

$$2H_2O+2SO_2+O_2=2H_2SO_4$$

It reduces an iodate to iodine but with excess of sulphur dioxide, iodine is further reduced to hydriodic acid.

$$2KIO_3+5SO_2+4H_2O=I_2+3H_2SO_4+2KHSO_4$$
$$I_2+SO_2+2H_2O=2HI+H_2SO_4$$

Sulphur dioxide reduces neutral solution of potassium permanganate ; thus if it is passed through pink solution of $KMnO_4$, the solution becomes colourless.

$$2KMnO_4+5SO_2+2H_2O=K_2SO_4+2MnSO_4+2H_2SO_4$$

Sulphur dioxide reduces acidified potassium dichromate solution ; thus if SO_2 is passed through $K_2Cr_2O_7$ solution acidified with sulphuric acid, the orange-yellow colour of the solution becomes green.

$$K_2Cr_2O_7+3SO_2+H_2SO_4=K_2SO_4+Cr_2(SO_4)_3+H_2O$$

Aqueous solution of the gas reduces hydrogen peroxide to water.

$$H_2SO_3+H_2O_2=H_2SO_4+H_2O$$

Ferric salts are reduced by sulphur dioxide to ferrous salts.

$$2FeCl_3+SO_2+2H_2O=2FeCl_2+2HCl+H_2SO_4$$

(vi) **Oxidising properties.** Under certain conditions, sulphur dioxide oxidises carbon to carbon dioxide.

$$SO_2+C=CO_2+S$$

The reaction is exothermic and takes place rapidly and almost completely at 1100°C.

In strongly acidic solution, it oxidises ferrous chloride to ferric chloride.

$$4FeCl_2+SO_2+4HCl=4FeCl_3+2H_2O+S$$

Hydrogen sulphide is oxidised to sulphur by sulphur dioxide.

$$2H_2S+SO_2=2H_2O+3S$$

An aqueous solution of SO_2 is reduced to H_2S by Zn and HCl.

$$H_2SO_3+3Zn+6HCl=H_2S+3ZnCl_2+3H_2O$$

Sulphur dioxide oxidises carbon monoxide to carbon dioxide when heated to 500°C in presence of a catalyst (bauxite).

$$SO_2+2CO=2CO_2+S$$

In presence of ultraviolet light, the aqueous solution of sulphur dioxide undergoes auto-oxidation reduction.

$$3H_2SO_3=2H_2SO_4+S+H_2O$$

(vii) Sulphur dioxide reacts with lead dioxide and sodium peroxide on being heated forming lead sulphate and sodium sulphate respectively.

$$PbO_2+SO_2=PbSO_4\ ;\ Na_2O_2+SO_2=Na_2SO_4$$

(viii) Phosphorus pentachloride reacts with sulphur dioxide forming thionyl chloride and phosphoryl chloride.

$$SO_2+PCl_5=SOCl_2+POCl_3$$

Explanation of oxidising and reducing properties of sulphur dioxide. The oxidising and reducing properties of sulphur dioxide can be explained as follows :

The common oxidation states in which sulphur atom can exist in its stable compounds are +6, +4 and −2. The highest positive oxidation state in which sulphur can exist in its compounds is +6 because it contains 6 electrons in its outermost shell. In sulphur dioxide sulphur atom exists in +4 oxidation state. Hence, in its reactions, sulphur atom is capable of transiting from +4 oxidation state to +6 oxidation state as well as from +4 oxidation state to 0 and −2 oxidation state. In reactions with oxidising agents, sulphur atom of sulphur dioxide goes from +4 oxidation to +6 oxidation state by losing electron. Consequently, in these reactions it acts as a reducing agent. On the other hand, in reactions with reducing agents sulphur atom of sulphur dioxide goes from +4 oxidation state to 0 and −2 oxidation states by accepting electrons. Hence, in these reactions it acts as an oxidising agent.

(ix) **Bleaching property.** Sulphur dioxide, in presence of moisture, bleaches many organic colouring substances to colourless compounds. Thus, it is used to bleach paper, straw, wool, silk and other articles which cannot be bleached by chlorine because chlorine destroys them. Some foods such as dried fruits are bleached by sulphur dioxide. Materials bleached by sulphur dioxide upon exposure to light and air sometimes regain their original colour.

In bleaching by sulphur dioxide, water is necessary and hence dry sulphur dioxide cannot bleach dry flowers. The bleaching property of it is explained by two theories : (i) It is due to the fact that sulphurous acid forms with organic colouring matter, unstable addition compounds which are colourless. The original colours of the materials are restored because of the gradual breakdown of the addition compounds. (ii) The bleaching is due to the reduction of coloured compound to colourless compound by nascent hydrogen formed by the reaction of sulphur dioxide with water.

$$SO_2+2H_2O=H_2SO_4+2H$$

$$\text{colouring matter} +2H \rightarrow \text{colourless matter}$$

Uses of sulphur dioxide. (i) Large quantities of sulphur dioxide are used in the manufacture of sulphuric acid and various sulphites. Calcium bisulphite $Ca(HSO_3)_2$ is used in the manufacture of paper pulp ; it dissolves lignin which holds together the fibres of cellulose in the wood.

(ii) It is used for bleaching straw, wool, silk, etc. It is also used as a disinfectant for killing the germs of many micro-organisms and for fumigation to destroy mould fungi in damp cellars and basements, wine barrels, fermentation tanks, etc.

(iii) It is used as a preservative for dried fruits. It is used as an *antichlor* for removing excess chlorine from bleached materials.

(iv) Sulphur dioxide finds use as a refrigerating agent, particularly in large commercial units.

(v) Liquid sulphur dioxide is a good solvent for many substances such as phosphorus, iodine, resins, etc.

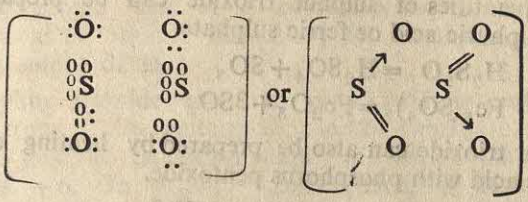
Tests. (i) Sulphur dioxide is detected by its characteristic pungent smell of burnt sulphur. (ii) It turns a piece of paper soaked with acidified solution of potassium dichromate green. (iii) It decolourises potassium permanganate solution.

When a sulphite is treated with dilute hydrochloric acid, SO_2 is evolved, which is recognised by the above tests.

When barium chloride solution is added to a solution of a sulphite, white precipitate of barium sulphite soluble in dilute hydrochloric acid is obtained.

Absorbent. Sulphur dioxide is absorbed by sodium hydroxide or potassium hydroxide.

Molecular structure. In the molecule of sulphur dioxide, sulphur atom is linked to one oxygen atom by a co-ordinate co-valent bond and to the other oxygen by two ordinary covalent bonds (double bond). Since the two oxygen atoms are identical, two equivalent electronic structures are possible for the sulphur dioxide molecule. The structure is, therefore, a resonance hydrid of these two forms. The situation is represented as follows :



Sulphur trioxide, SO_3

It seems probable that sulphur trioxide was known in the seventeenth century as "philosophical salt". It was called by K. W. Scheele the anhydride of sulphuric acid.

Preparation. (i) By the direct union of sulphur dioxide and oxygen. Sulphur trioxide can be prepared by the direct combination of sulphur dioxide and oxygen.

$$2SO_2+O_2 \rightleftharpoons 2SO_3$$

The reaction is reversible and takes place very slowly under ordinary conditions. However, in the presence of catalyst such as finely divided platinum or vanadium pentoxide and at 434°C, the reaction proceeds rapidly and an optimum yield of sulphur trioxide is obtained. At temperatures higher than 434°C, the yield of sulphur trioxide decreases and at 1000°C, the yield is zero.

Sulphur trioxide can be prepared in the laboratory by an arrangement shown in fig. 9.5. Oxygen and sulphur dioxide are dried by passing them through conc. H_2SO_4 in a jar (a). The mixture of dried gases then passes into the tube (b) containing platinised asbestos (asbestos coated with finely divided platinum)

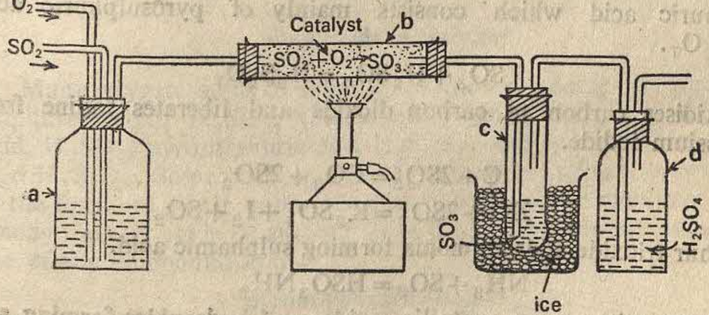


Fig. 9.5

which is heated by a gas burner. Sulphur dioxide combines with oxygen in the tube forming sulphur trioxide which passes together with unreacted gases into the tube (c) cooled by ice and water. Part of sulphur trioxide condenses here and the rest passes into the bottle (d) where it reacts with water producing sulphuric acid.

(ii) Small quantities of sulphur trioxide can be prepared by distilling pyrosulphuric acid or ferric sulphate.

$$H_2S_2O_7 = H_2SO_4 + SO_3$$
$$Fe_2(SO_4)_3 = Fe_2O_3 + 3SO_3$$

(iii) Sulphur trioxide can also be prepared by heating concentrated sulphuric acid with phosphorus pentoxide.

$$H_2SO_4 + P_2O_5 = SO_3 + 2HPO_3$$

Properties. (A) Physical properties : At ordinary temperatures, pure sulphur trioxide is a colourless mobile liquid which boils at 44·5°C and freezes at 16·8°C into a transparent crystalline mass (α-form). The solid sulphur trioxide exists in two forms. The α-form consists of colourless needles which melt at 16·8°C. These crystals fume in moist air and on standing gradually change into long silky crystals which sublime at 50°C without melting. This modification is known as β-sulphur trioxide which has a molecular weight corresponding with the formula $(SO_3)_x$. The liquid fumes strongly in moist air.

(B) Chemical properties : Sulphur trioxide dissociates appreciably at about 400°C and the higher the temperature, the further it proceeds :

$$2SO_3 \rightleftharpoons 2SO_2 + O_2$$

Sulphur trioxide dissolves in water with hissing sound evolving a large amount of heat and sulphuric acid is produced.

$$SO_3 + H_2O = H_2SO_4$$

It dissolves readily in sulphuric acid forming oleum or fuming sulphuric acid which consists mainly of pyrosulphuric acid, $H_2S_2O_7$.

$$SO_3 + H_2SO_4 = H_2S_2O_7$$

It oxidises carbon to carbon dioxide and liberates iodine from potassium iodide.

$$C + 2SO_3 = CO_2 + 2SO_2$$
$$2KI + 2SO_3 = K_2SO_4 + I_2 + SO_2$$

Sulphur trioxide adds ammonia forming sulphamic acid.

$$NH_3 + SO_3 = HSO_3NH_2$$

It reacts with many metallic oxides and hydroxides forming sulphates and bisulphates.

$$BaO + SO_3 = BaSO_4$$
$$NaOH + SO_3 = NaHSO_4$$

Sulphur trioxide adds to hydrochloric acid in presence of sulphuric acid forming chlorosulphonic acid.

$$SO_3+HCl=HSO_3Cl$$

Chlorosulphonic acid is a colourless liquid which finds wide applications in organic chemistry, for example, in the preparation of sulpha drugs.

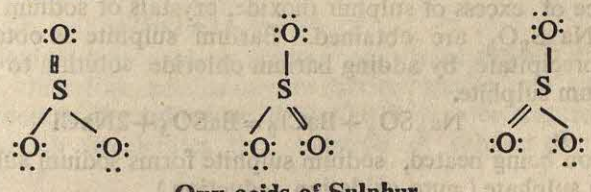
Sulphur trioxide acts only as an oxidising agent. There are six electrons in the outermost shell of sulphur atom. Hence, the highest positive oxidation state in which sulphur atom can exist is $+6$. In sulphur trioxide, sulphur atom exists in $+6$ oxidation state. Hence, it cannot act as a reducing agent. On the other hand, it can act as a powerful oxidising agent because in these reactions, sulphur atom of sulphur trioxide can go from $+6$ oxidation state to $+4$, 0 or -2 oxidation states by accepting electrons.

Molecular formula. When heated to 1000°C, sulphur trioxide decomposes completely into sulphur dioxide and oxygen.

$$2SO_3=2SO_2+O_2$$

Two volumes of sulphur trioxide yield two volumes of sulphur dioxide and one volume of oxygen. Hence, its formula is $(SO_3)_x$. The vapour density of the sulphur trioxide shows that its formula must be SO_3.

Molecular structure. Three equivalent electronic structures of sulphur trioxide are possible. Its structure is a rosonance hybrid of these three forms.



Oxy-acids of Sulphur

Many oxygen acids of sulphur are known. Some of them are sulphurous acid, H_2SO_3, thiosulphuric acid, $H_2S_2O_3$, sulphuric acid, H_2SO_4, pyrosulphuric acid $H_2S_2O_7$, and peroxy disulphuric acid $H_2S_2O_8$. Some of these acids are unstable and are known only in the form of their salts. Sulphuric acid is the most important among the oxy-acids of sulphur since it has the greatest industrial use of any compound known.

Sulphurous acid, H_2SO_3

Sulphurous acid is a very unstable compound and is known only in aqueous solution. It is formed when sulphur dioxide is dissolved in water. $SO_2+H_2O\rightleftharpoons H_2SO_3$

Attempts to isolate sulphurous acid from water result in their total decomposition and an accompanying evolution of sulphur dioxide. When sodium sulphite is treated with concentrated sulphuric acid, sulphurous acid is not formed and instead sulphur dioxide is evolved.

$$Na_2SO_3+H_2SO_4=Na_2SO_4+SO_2+H_2O$$

Solution of sulphurous acid absorbs oxygen from air forming sulphuric acid and hence they should be kept in air-tight vessel.

$$2H_2SO_3+O_2=2H_2SO_4$$

In sulphurous acid, sulphur atom exists in +4 oxidation state. Sulphur can exist in −2, +4 and +6 oxidation states in its stable compounds. Hence, sulphurous acid possesses both oxidising and reducing properties. At 150°C, it undergoes auto-oxidation-reduction.

$$3H_2\overset{+4}{S}O_3 \rightleftharpoons 2H_2\overset{+6}{S}O_4+\overset{0}{S}+H_2O$$

Sulphites and bisulphites. Sulphurous acid forms two series of salts ; the normal salts are called sulphites and the acid salts are called hydrogen sulphites or bisulphites.

Sodium sulphite is prepared as follows : A solution of caustic soda is divided into two equal parts. One part is saturated with sulphur dioxide when a solution of sodium hydrogen sulphite $NaHSO_3$, is formed. This is then mixed with the other half of sodium hydroxide solution. The resulting solution on evaporation yields the crystals of normal sodium sulphite, $Na_2SO_3, 7H_2O$. Sodium bisulphite, $NaHSO_3$ has not been isolated in the solid state. If the solution of sodium hydrogen sulphate is evaporated in presence of excess of sulphur dioxide, crystals of sodium metabisulphite $Na_2S_2O_5$ are obtained. Barium sulphite is obtained as a white precipitate by adding barium chloride solution to a solution of sodium sulphite.

$$Na_2SO_3+BaCl_2=BaSO_3+2NaCl$$

Upon being heated, sodium sulphite forms sodium sulphide and sodium sulphate (auto-oxidation reduction).

$$4Na_2SO_3=3Na_2SO_4+Na_2S$$

Sulphites are decomposed by dilute acids evolving sulphur dioxide.

$$Na_2SO_3+2HCl=2NaCl+SO_2+H_2O$$

Uses of sulphites and bisulphites. Sulphites find employment in the laboratory and photographic darkroom. Sodium metabisulphite $Na_2S_2O_5$ is used in photography as a developer. Huge quantities of calcium bisulphite $Ca(HSO_3)_2$ are used in the sulphite process for manufacturing paper. Sulphites are used in electroplating and in the removal of oxygen from boiler water. The solutions of the sulphites are employed in separating the protein and carbohydrate portion of the wheat and other grains.

Sulphuric Acid, Oil of Vitriol, H_2SO_4

Sulphuric acid was made in the fifteenth century by distilling green vitriol (ferrous sulphate) from which it derives its name "oil of vitriol" or "vitriolic acid".

$$2(FeSO_4, 7H_2O)=Fe_2O_3+H_2SO_4+SO_2+13H_2O$$

In 1740 Ward, a quack doctor of England manufactured sulphuric acid by burning a mixture of sulphur and nitre over a dish of water under a glass bell. This process is the basis for the development of lead chamber process which is now largely used for the manufacture of ordinary sulphuric acid. The "contact process" for manufacturing fuming sulphuric acid was developed at the end of the 19th century and was largely owing to the labours of Messel and Winkler, (1875) ; Knietsch and Krauss (1901).

Free sulphuric acid is found in traces in mineral springs and rivers whose waters have been in contact with beds of pyrites.

$$2FeS_2+7O_2+2H_2O=2FeSO_4+2H_2SO_4$$

It is found in rain water of towns where coal is burnt. It is widely distributed in nature in combination as sulphates.

Laboratory preparation of sulphuric acid. In the laboratory preparation, sulphur dioxide is oxidised to sulphuric acid by the action of air, oxides of nitrogen NO and NO_2, and water. Nitrogen dioxide reacts with sulphur dioxide forming sulphur trioxide which reacts with water yielding sulphuric acid.

$$SO_2+NO_2=SO_3+NO$$

$$SO_3+H_2O=H_2SO_4$$

Yielding part of its oxygen to sulphur dioxide, nitrogen dioxide is converted into nitric oxide which combines with oxygen of air to form nitrogen dioxide again.

$$2NO+O_2=2NO_2$$

Nitrogen dioxide then oxidises further quantity of sulphur dioxide. Nitric oxide, therefore, acts as oxygen carrier and is not used up in the production of sulphuric acid so that it may be regarded as a catalyst which accelerates the oxidation of sulphur dioxide to sulphur trioxide.

Also there occurs a series of complicated reactions which are not definitely understood. By one of such reactions, nitrosylsulphuric acid is formed by the reaction between sulphur dioxide and oxides of nitrogen in the presence of air and water.

$$2SO_2+NO+NO_2+H_2O+O_2=2SO_2(OH)(NO_2)$$

In presence of excess of water, nitrosylsulphuric acid decomposes to form sulphuric acid.

$$2(SO_2)(OH)(NO_2)+H_2O=2H_2SO_4+NO+NO_2$$

The oxides of nitrogen are regenerated and used over again. If too little water is present white crystals of nitrosylsulphuric acid called chamber crystals are deposited. But in practice chamber crystals are not permitted to be formed.

A large flask (A) is fitted with a cork through which pass four inlet tubes and a small outlet tube. Three of the inlet tubes come from wash-bottles containing concentrated sulphuric acid and the fourth from a flask in which water is boiled. The wash-bottle (C) is connected with a siphon of liquid sulphur dioxide and the other two (B) and (D) with gas holders containing nitric oxide and oxygen respectively. Oxygen, nitric oxide and sulphur dioxide and a small amount of steam are then passed into flask (A) when white crystals of nitrosylsulphuric acid are formed. More steam is then passed into the flask (A) by boiling water into the small flask (E) when white crystals react with the steam liberating red oxides of nitrogen and forming fairly concentrated sulphuric acid which collect at the bottom of the flask. The complex reactions that take place can be represented as

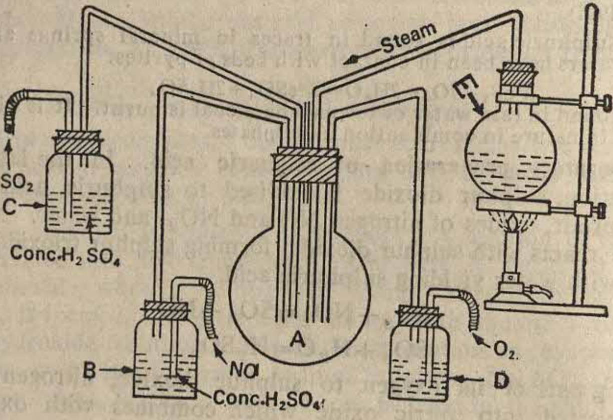


Fig. 9.6

$$2SO_2+NO+NO_2+O_2+H_2O=2SO_2(OH)(NO_2)$$
$$2SO_2(OH)(NO_2)+H_2O=2H_2SO_4+NO+NO_2$$

Properties of sulphuric acid. (A) Physical properties : Pure 100% sulphuric acid is a heavy colourless oily liquid which freezes at 10·5°C into a solid crystalline mass. It is almost a non-conductor of electricity but its aqueous solution is a good conductor of electricity. When concentrated acid is dissolved in water, a large amount of heat is evolved. The concentrated sulphuric acid which is used as a reagent contains about 95% H_2SO_4 and has a specific gravity of 1·84. The anhydrous acid on being heated loses sulphur trioxide formed as a result of the dissociation.

$$H_2SO_4 \rightleftharpoons H_2O+SO_3$$

The liberation of sulphur trioxide continues until a solution containing 98·3 per cent sulphuric acid results. This solution called the constant boiling mixture of sulphuric acid and water boils at 338°C with no further change in composition.

(B) **Chemical properties :** (i) **Thermal stability.** If the vapour of sulphuric acid is passed through a red-hot silica tube or when sulphuric acid is dropped on heated pumice stone, it is decomposed into water vapour, sulphur dioxide and oxygen.

$$2H_2SO_4 = 2H_2O + 2SO_2 + O_2$$

(ii) **Dehydrating action.** Concentrated sulphuric acid has a great affinity for water. Much heat is evolved when the acid is added to water due to the formation of hydrates. The hydrates such as H_2SO_4, H_2O ; $H_2SO_4, 2H_2O$ and $H_2SO_4, 4H_2O$ can be isolated in the solid form from the solution at low temperatures. The hydrate H_2SO_4, H_2O melts at -38°C and $H_2SO_4, 4H_2O$ at -27°C.

Concentrated sulphuric acid attracts moisture strongly and hence is used for drying gases which do not react with the acid and in desiccators. It abstracts the elements of water from some organic compounds such as sugar, alcohol, formic acid, etc.

$$C_{12}H_{22}O_{11} + 11H_2SO_4 = 12C + 11H_2SO_4, H_2O$$
$$C_2H_5OH + H_2SO_4 = C_2H_4 + H_2SO_4, H_2O$$
$$HCOOH + H_2SO_4 = CO + H_2SO_4, H_2O$$

The dehydrating action of the acid is used to eliminate water in many chemical reactions, such as nitration in the manufacture of dyes and explosives. This property also accounts for its destructive effect on plant and animal tissues.

(iii) **Acid properties.** Sulphuric acid shows the usual properties of a dibasic acid. It ionises in two stages and forms two series of salts : normal and acid salt, e.g., Na_2SO_4 and $NaHSO_4$

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$$
$$HSO_4^- \rightleftharpoons H^+ + SO_4^{--}$$

It is a strong acid but in dilute solution it is weaker than HCl and HNO_3. At high temperatures, sulphuric acid displaces HCl and HNO_3 from their salts.

$$NaCl + H_2SO_4 \rightleftharpoons NaHSO_4 + HCl$$
$$NaNO_3 + H_2SO_4 \rightleftharpoons NaHSO_4 + HNO_3$$

Theoretically, these reactions are reversible but as HCl and HNO_3 are much more volatile than H_2SO_4 they are driven off when the mixtures are warmed and the reactions proceed to the right. Some typical acid reactions of sulphuric acid are.

$$NaOH + H_2SO_4 = NaHSO_4 + H_2O$$
$$NaOH + NaHSO_4 = Na_2SO_4 + H_2O$$

$$H_2SO_4+2NH_3=(NH_4)_2SO_4$$

A solution of Na_2SO_4 in water is essentially neutral but a solution of $NaHSO_4$ is strongly acidic because of the appreciable ionisation of the HSO_4^- ion.

(iv) **Oxidising properties.** In sulphuric acid, the sulphur atom exists in its highest positive oxidation state (+6). Consequently, it acts as a strong oxidising agent and fails to act as a reducing agent.

(a) Metals which are more electropositive than hydrogen are oxidised by cold dilute sulphuric acid due to the displacement of hydrogen.

$$Fe+H_2SO_4=FeSO_4+H_2$$
$$Zn+H_2SO_4=ZnSO_4+H_2$$

Metals below hydrogen in the electrochemical series such as copper, silver, lead and mercury are not attacked by cold dilute sulphuric acid. Concentrated sulphuric acid oxidises almost all the metals when heated ; in such reactions hydrogen is not evolved and the acid is usually reduced to sulphur dioxide but it may be reduced to free sulphur or to a sulphide.

$$Cu+2H_2SO_4=CuSO_4+SO_2+2H_2O$$
$$Zn+2H_2SO_4=ZnSO_4+SO_2+2H_2O$$

Due to the activity of zinc, the following reactions occur simultaneously with the latter.

$$3Zn+4H_2SO_4=3ZnSO_4+S+4H_2O$$
$$4Zn+5H_2SO_4=4ZnSO_4+H_2S+4H_2O$$

(b) Non-metals are usually oxidised by sulphuric acid to their oxides. Thus, hydrogen is slowly oxidised to water by concentrated sulphuric acid.

$$H_2+H_2SO_4=2H_2O+SO_2$$

If concentrated sulphuric acid is heated with charcoal, the latter is oxidised to carbon dioxide while sulphuric acid is reduced to sulphur dioxide.

$$2H_2SO_4+C=CO_2+2SO_2+2H_2O$$

Similarly, sulphur is oxidised to sulphur dioxide.

$$S+2H_2SO_4=3SO_2+2H_2O$$

Hot concentrated sulphuric acid oxidises phosphorus to phosphoric and phosphorous acid while it is reduced to sulphur dioxide and sulphur.

$$2P+3H_2SO_4=2H_3PO_3+3SO_2$$
$$2P+3H_2SO_4=2H_3PO_4+S+2SO_2$$

(c) Sulphuric acid oxidises the bromides and iodides. The hydrobromic and hydriodic acid first formed are oxidised to bromine and iodine respectively.

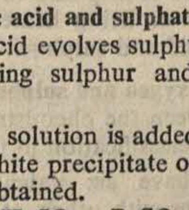
$$H_2SO_4+2HBr=Br_2+SO_2+2H_2O$$
$$H_2SO_4+2HI=2H_2O+SO_2+I_2$$

(v) Concentrated sulphuric acid reacts with phosphorus pentachloride forming chlorosulphonic acid and sulphuryl chloride.

$$SO_2(OH)_2+PCl_5=SO_2(OH)Cl+POCl_3+HCl$$
$$SO_2(OH)Cl+PCl_5=SO_2Cl_2+POCl_3+HCl$$

Uses of sulphuric acid. Sulphuric acid is one of the most important industrial chemicals. Its uses are numerous. Immense quantities of the acid are used in the production of fertiliser, e.g., ammonium sulphate and superphosphate of lime. Sulphuric acid is employed extensively in the refining of petroleum and in the removal of impurities from crude oil, gasoline, and kerosene. It is also employed in the manufacture of explosives, alums, phosphorus, dyestuffs, drugs and disinfectants. Large quantities of the acid are used in the manufacture of a great variety of chemicals such as textiles, plastics, coal-tar products, metal sulphates and other acids. It is used as an electrolyte in lead-storage batteries. It is employed in metallurgy and in the pickling of steel. Oleum is used in the manufacture of edible products; for filling accumulators and in the oxidation and sulphonation reactions in organic chemistry.

Molecular structure of H_2SO_4. The four oxygen atoms are arranged tetrahedrally about the central sulphur atom.



Tests of sulphuric acid and sulphate. (i) If heated with copper turnings, sulphuric acid evolves sulphur dioxide which is recognised by its smell of burning sulphur and decolourisation of $KMnO_4$ solution.

(ii) When $BaCl_2$ solution is added to a solution of sulphuric acid or a sulphate, white precipitate of brium sulphate insoluble in dil or conc. HCl is obtained.

$$BaCl_2+H_2SO_4=BaSO_4+2HCl$$

(iii) A small quantity of a sulphate is mixed with sodium carbonate and the mixture is heated on charcoal under the reducing flame. Sulphate is reduced to sulphide.

$$ZnSO_4+4C=ZnS+4CO$$

The reduced mass is treated with dil. HCl when H_2S is evolved which turns lead acetate paper black.

$$ZnS+2HCl=ZnCl_2+H_2S$$

$$Pb(CH_3COO)_2+H_2S=PbS+2CH_3COOH$$

APPENDIX

(1) **Differences between oxygen and sulphur.** Oxygen and sulphur are first and second members in group VIA of the periodic classification. The properties of oxygen and its compounds are in many respects different from those of sulphur and its compounds. The chief points of differences are given below.

(i) At ordinary temperature, oxygen is a colourless, odourless gas while sulphur is a yellow solid. The molecule of oxygen is O_2 but that of sulphur is S_8.

(ii) In oxygen, both metals and non-metals burn fiercely. Sulphur, on the other hand, is a combustible solid.

(iii) In all compounds except F_2O*, oxygen exhibits the oxidation number of -2 only but sulphur can exist in the oxidation states of -2, $+4$ and $+6$. Thus, in SF_6 and H_2SO_4 sulphur is positively hexavalent. Oxygen does not form any compound which is analogous to sulphites and sulphates.

(iv) Compounds of oxygen are frequently associated whereas corresponding sulphur compounds are not. For example, water which is a liquid at ordinary temperature is associated, $(H_2O)_n$ but hydrogen sulphide is a gas composed of simple molecules, H_2S.

(v) Sulphur forms compounds which are more acidic than the corresponding compounds of oxygen. Thus, water is neutral but hydrogen sulphide H_2S is a weak acid.

(vi) Chlorides of oxygen are explosive, they react directly with water to form acids. Chlorides of sulphur, on the other hand, are not explosive. They dissociate on being heated. They react with water forming hydrochloric acid and sulphur.

(2) **Similarities between oxygen and sulphur.** The following are the important similarities between the chemistry of oxygen and that of sulphur which justify their classification in the same group.

(i) Both the elements have six valence electrons, ns^2np^4. Hence, by sharing two electrons with other atoms, they can form two covalent bonds. Thus, in water H_2O and hydrogen sulphide, H_2S, both oxygen and sulphur form two covalent bonds. Again, both of them can accept two electrons, forming bivalent anions. For example, in $Na_2^{++}O^{--}$ and $Na_2^{++}S^{--}$, both oxygen and sulphur exist in di-electrovalent state.

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* In F_2O, the oxidation number of oxygen is $+2$.

(ii) Oxides and sulphides of metals and non-metals exhibit great similarities in their properties and reactions ; thus

$$Sb_2O_3 + 6HCl = 2SbCl_3 + 3H_2O$$

$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S$$

$$FeO + 2HCl = FeCl_2 + H_2O$$

$$FeS + 2HCl = FeCl_2 + H_2S$$

Similarly, carbon disulphide, CS_2 is very similar to carbon dioxide CO_2. Thus, CS_2 reacts with sodium hydroxide forming sodium thiocarbonate Na_2CS_3 which is analogous to sodium carbonate Na_2CO_3 formed by the reaction between CO_2 and NaOH. Stannic sulphide, SnS_2 which is similar to stannic oxide, SnO_2 reacts with ammonium sulphide, $(NH_4)_2S$, forming ammonium thiostannate, $(NH_4)_3SnS_3$ which is similar to sodium stannate, Na_3SnO_3 formed by the reaction between SnO_2 and Na_2O.

(iii) Both oxygen and sulphur occur in the free state in nature. Both of them exist in allotropic modifications.

(3) To prove that sulphuric acid contains sulphur, oxygen and hydrogen.

A flask fitted with a dropping funnel is half filled with pumice stone. The flask is heated strongly and concentrated sulphuric acid is allowed to fall drop by drop on the pumice stone when it decomposes into water, sulphur dioxide and oxygen.

$$2H_2SO_4 = 2H_2O + 2SO_2 + O_2$$

The mixture of gases are passed through a U-tube (i) cooled by cold water in which steam condenses to water, then through another U-tube (ii) cooled in a freezing mixture in which sulphur dioxide condenses to a liquid and finally oxygen is collected in a gas-jar by the displacement of water.

The liquid in U-tube (i) turns anhydrous copper sulphate blue. Hence, it is water. Again, on treating this liquid with metallic sodium, hydrogen is evolved.

The gas evolved on evaporation of the liquid in U-tube (ii) is passed through water and the solution is heated in a sealed tube to 150°C when a deposit of free sulphur is obtained. It burns in air giving smell of burning sulphur and dissolves in CS_2.

The gas in the jar rekindles glowing chip of wood, produces brown fumes with nitric oxide and is absorbed by alkaline pyrogallate solution. Hence, it is oxygen.

Sulphuric acid, therefore, contains hydrogen, sulphur and oxygen.

(4) **To prove that sulphur dioxide contains sulphur.** Saturated solution of sulphur dioxide in water is heated at 150°C in a closed vessel when yellow precipitates are obtained. The precipitates are filtered and dried. It dissolves in carbon disulphide. It burns in oxygen to form a gas having smell of burning sulphur. The gas turns acidified potassium dichromate solution green. Hence, the yellow precipitate is sulphur and it has come from sulphur dioxide. Therefore, sulphur dioxide contains sulphur.

(5) **To prove that hydrogen sulphide contains hydrogen and sulphur.** Pure and dry hydrogen sulphide is collected in a gas-jar and is burnt in a limited supply of oxygen. A yellow solid is deposited in the jar. The solid is soluble in carbon di-sulphide. It burns in oxygen to give a gas having smell of burning sulphur; the gas turns acidified potassium dichromate solution green. Hence, the yellow solid is sulphur and it has come from hydrogen sulphide. Hence, hydrogen sulphide contains sulphur.

A few c.c. of pure and dry hydrogen sulphide is collected into a bent tube by the displacement of mercury and a piece of tin is introduced into a horizontal portion of the tube. The piece of tin is heated from the outside when it reacts with hydrogen sulphide liberating a gas and a solid (tin sulphide). The gas is absorbed in heated palladium and burns in oxygen with a blue flame producing water. Hence, the gas is hydrogen. Hence, hydrogen sulphide contains hydrogen.

EXERCISES

1. Give the names and formulas of principal natural sources of sulphur. Describe the Frasch process of mining sulphur.

2. Discuss and describe the methods employed for the extraction of sulphur. Describe the different allotropic modifications of sulphur. Is the conversion from rhombic sulphur to monoclinic sulphur endothermic or exothermic? Explain.

3. Which allotrope of sulphur is stable at about 25°C? Describe the physical and chemical properties of this allotrope. Explain what happens when sulphur is heated slowly from room temperature to its boiling point. What is plastic sulphur? How is it obtained?

4. Starting from sulphur, how would you prepare (a) sodium bisulphite (b) hydrogen sulphide (c) sodium thiosulphate? (d) ferrous sulphide (e) sulphur dioxide and (f) sodium sulphate? "Sulphur is in many respects chemically analogous to oxygen"—Discuss.

5. How is hydrogen sulphide prepared in the laboratory? How is the gas purified? How would you show that (a) the gas contains hydrogen and sulphur (b) its molecular formula is H_2S? [Cal., '53]

6. Discuss the chemical properties of gaseous hydrogen sulphide and of its aqueous solution.

7. (a) How is pure hydrogen sulphide obtained in the laboratory?

(b) Explain why nitric acid cannot be used for preparing hydrogen sulphide. How would you show that the gas is (i) a reductant and (ii) a weak dibasic acid ?

Write equations for the burning of hydrogen sulphide in (i) a limited supply of oxygen and (ii) excess of oxygen.

8. How would you prepare sulphur dioxide in the laboratory ? How would you prove that the molecular formula of sulphur dioxide is SO_2 and not S_8O_{16} ?

What is the action of SO_2 on H_2S ? Which one is the oxidant in the reaction ?

What reactions can occur between sulphur dioxide and (i) nitric acid (ii) iodic acid (iii) phosphorus pentachloride (iv) potassium permanganate (v) lead dioxide (vi) sodium carbonate and (vii) milk of lime ?

9. Describe the industrial preparation of sulphur dioxide. How is it converted into sulphur trioxide for the manufacture of sulphuric acid by contact process ?

How would you convert sulphur dioxide into (i) S (ii) $SOCl_2$ and (iii) SO_2Cl_2.

10. How is sulphur converted into sulphuric acid ? What is oleum ?

11. Discuss the chemical properties of sulphuric acid ? How would you prove that it contains sulphur, hydrogen and oxygen ? What is (a) fuming sulphuric acid, (b) plastic sulphur and (c) oil of vitriol ?

12. Prove experimentally that sulphuric acid is (i) an acid (ii) a dehydrating agent (iii) an oxidant. Describe the reaction between sulphuric acid and (i) sulphur (ii) copper (iii) charcoal and (iv) lead. State the uses of sulphuric acid.

13. Given an aqueous solution known to contain either sulphate or sulphide ion, how would you proceed to find out which is present ?

14. What happens when

- (a) copper turnings are heated with strong sulphuric acid.
- (b) the gaseous product formed by burning iron pyrite is passed into the solution of sodium hydroxide.
- (c) phosphorus pentachloride is treated with concentrated sulphuric acid.
- (d) hydrogen sulphide is passed through acidified solution of copper sulphate.
- (e) a mixture of sulphur dioxide and oxygen is passed over heated platinum gauze.
- (f) sulphur is heated with concentrated nitric acid.
- (g) potassium carbonate is fused with sulphur.
- (h) conc. H_2SO_4 is heated with charcoal.
- (i) sulphur is heated with conc. H_2SO_4.
- (j) phosphorus is heated with conc. H_2SO_4.
- (k) sodium iodide is heated with conc. H_2SO_4.

15. Explain the following statements :

(a) Sulphur dioxide acts both as an oxidising and a reducing agent while sulphur trioxide acts only as an oxidising agent.

(b) Sulphurous acid behaves both as oxidising agent and reducing agent while sulphuric acid acts only as oxidising agent.

(c) Sulphurous acid undergoes auto oxidation-reduction while sulphuric acid fails to exhibit this phenomenon.

(d) An oxygen atom can readily be attached to sulphur dioxide molecule.

(e) Sulphuryl choloride (SO_2Cl_2) is formed by the action of anhydrous sulphur dioxide on anhydrous chlorine while HCl and H_2SO_4 are formed when aqueous solution of SO_2 react with chlorine.

(f) In volcanic region, sulphur deposits are usually found.

16. A solid compound of iron (X) is treated with dil. H_2SO_4 when a bad smelling gas (Y) is evolved. The gas when passed through alkaline solution of zinc chloride gives a white precipitate (Z). The precipitate (Z) on treatement with dil. HCl gives a gas which turns lead acetate paper black. Identify the compounds (X), (Y) and (Z).

[Ans. X → FeS, Y → H_2S and Z → ZnS]

17. A solid compound of sodium (A) when heated with powdered charcoal yields another solid (B) and a gas (C). The gas (C) burns in oxygen forming another gas (D) which turns lime-water milky. The residue (B) dissolves in water giving an alkaline solution which forms purple colouration with sodium nitroprusside solution. Identify the compounds (A), (B), (C) and (D). [Ans. A → Na_2SO_4, B → Na_2S, C → CO and D → CO_2]

CHAPTER X

THE HALOGEN FAMILY

Elements	Symbol	Atomic weight	Atomic number	Distribution of extranuclear electrons in neutral atoms of the elements				
				K 1s	L 2s 2p	M 3s 3p 3d	N 4s 4p 4d 4f	O 5s 5p
Fluorine	F	19·00	9	$1s^2$	$2s^2$ $2p^5$			
Chlorine	Cl	35·457	17	$1s^2$	$2s^2$ $2p^6$	$3s^2$ $3p^5$		
Bromine	Br	79·916	35	$1s^2$	$2s^2$ $2p^6$	$3s^2 3p^6$ $3d^{10}$	$4s^2 4p^5$	
Iodine	I	126·91	53	$1s^2$	$2s^2$ $2p^6$	$3s^2 3p^6 3d^{10}$	$4s^2 4p^6 4d^{10}$	$5s^2$ $5p^5$

General features of the halogens. The elements, fluorine, chlorine, bromine, iodine and astatine constitute the group VIIA of the periodic table. These elements are known as the halogens (Greek. *halos* : the sea-salt producer), because they react readily with the lighter metals forming typical salts such as NaCl.

The atoms of the halogens have seven electrons in their outermost shell. Being one electron short of an octet, the halogen atoms gain one electron very readily, passing into negative univalent ions called halide ions ; thus

$$X+e \rightarrow X^- \text{ and } X_2+2e \rightarrow 2X^- \text{ where } X=F, Cl, Br, \text{ and } I.$$

Hence, the negative valency of the halogen is 1. The electronic configurations of the halide ions correspond to that of noble gases. The halogen atoms can also attain the octet by sharing an electron pair with the atoms whose valence electrons are too firmly bound to permit transference to occur. In the gaseous state, the halogens exist as diatomic molecule ; a covalent bond joins the two halogen atoms :

$$:\underset{\cdot\cdot}{\overset{\cdot\cdot}{X}}\cdot \quad + \quad \cdot\underset{\cdot\cdot}{\overset{\cdot\cdot}{X}}: \rightarrow :\underset{\cdot\cdot}{\overset{\cdot\cdot}{X}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{X}}: \qquad (X-X \text{ or } X_2)$$

The halogen molecules do not undergo thermal dissociation but they take part readily in chemical combination with other elements. The order of activity is fluorine, chlorine, bromine and iodine ; fluorine is the most reactive and displays an unparallel readiness to enter into chemical combination with other elements. Halogens form compounds with hydrogen known as the hydrides of halogens whose aqueous solutions are acids ; but in the gaseous state they are covalent compounds. They also react with other non-metals such as oxygen, sulphur, phosphorus, nitrogen, silicon and carbon, forming covalent compounds. Fluorine brings about the highest covalency of an element with which it forms compounds but the covalency of fluorine never exceeds 1. For example, the maximum covalency of sulphur, arsenic and iodine is found in their compounds, SF_6, AsF_5 and IF_7 respectively but in these compounds fluorine exhibits the covalency of 1.

As can be seen from their electronic structure, the maximum possible positive valency of the halogens is seven. However, only chlorine, bromine and iodine are capable of forming compounds in which they exist in variety of positive states of oxidation. Iodine has the greatest tendency among the halogens towards the existence in the positive oxidation state.

Because of the fact that halogen atoms can readily accept an electron from metallic elements, they are regarded as typical non-metals. Fluorine is the most electronegative of all the elements and hence it is most non-metallic in its behaviour. With increase in atomic number from fluorine to iodine, the halogens remain predominantly non-metallic elements, but nevertheless show a progressive trend towards metallic character. Thus, there are a few compounds of bromine in which it exists as Br^+ ion whereas iodine forms compounds such as $I(PO_4)$, $I_2(SO_4)_3$, $I(NO_3)$, etc., in which the iodine atom is playing, beyond doubt, the role of a cation. Again the fluoride ion F^- is the most stable while the iodide ion I^- is the least stable ; electron once accepted by fluorine atom is most difficult to remove while an electron can easily be removed from an iodine atom. Fluorine atom is the strongest known oxidising agent because it has the greatest ability to remove electrons from other atoms. Hence, greatest difficulty is encountered in oxidising the fluoride ion while iodide ion can easily be oxidised. In fact, iodides are better reducing agents than other halides. Since the attraction for electron is strongest in fluorine and weakest in iodine ; fluorine will, therefore, expel chlorine from combination with a metal, chlorine will expel bromine and bromine will expel iodine :

$$2KCl + F_2 = 2KF + Cl_2 \quad \text{or} \quad 2Cl^- + F_2 = 2F^- + Cl_2$$

$$2KBr + Cl_2 = 2KCl + Br_2 \quad \text{or} \quad 2Br^- + Cl_2 = 2Cl^- + Br_2$$

Fluorine, F

Since the element is extremely reactive, it does not occur free in nature. It occurs in the combined state in minerals such as fluorspar or fluorite CaF_2, fluorapatite, $CaF_2, 3Ca_3(PO_4)_2$ cryolite Na_3AlF_6. In small quantites, it is present in bones, in the enamel of teeth and in sea water. Faint traces of fluoride ion should be present in the drinking water of children otherwise their teeth will not be properly resistant to decay.

History of isolation of fluorine. Scheele in 1771 prepared hydrofluoric acid by heating fluorspar with sulphuric acid and named it the fluoric acid. He found that the fluoric acid has the property of attacking glass. In 1813, Davy established that hydrofluoric acid is analogous to hydrochloric acid and is a compound of hydrogen and an unknown element similar to chlorine. The unknown element was named 'fluorine' by analogy with chlorine. Davy attempted to isolate fluorine by the electrolysis of aqueous solution of hydrogen fluoride but his attempt failed. He obtained hydrogen and oxygen instead of hydrogen and the new element as the products of electrolysis. Similar attempts made by Gore, Fremy and others for isolating the element were also unsuccessful. The reasons for their failure are as follows :

(i) When an aqueous solution of hydrofluoric acid is electrolysed, oxygen is liberated at the anode and hydrogen at the cathode because fluorine reacts with water immediately after its liberation from HF.

$$2H_2O+2F_2=4HF+O_2$$

As a result, water alone is decomposed.

(ii) The anhydrous hydrofluoric acid does not conduct electricity and it cannot, therefore, be eleotrolysed.

(iii) Chemically, fluorine is extremely reactive ; it attacked all the materials of the apparatus in which it was tried to be isolated and no vessels seemed to be capable of resisting its chemical action.

(iv) Both fluorine and hydrofluoric acid are extremely poisonous. The problem was finally solved by Moissan who found that when potassium fluoride KF is dissolved in the liquid hydrogen fluoride, the solution conducts electric current. He isolated fluorine in 1886 by the electrolysis of this solution in a U-tube made of platinum-iridium alloy and fitted with electrodes of the same alloy.

Preparation of fluorine. (i) **Moissan's method.** In this method, a solution of potassium fluoride in liquid hydrogen fluoride is electrolysed ; hydrogen is evolved at the cathode, and fluorine at the anode :

$$KF+HF=KHF_2$$
$$2KHF_2=2HF+2KF\ ;\ 2KF\rightleftharpoons 2K^++2F^-$$

$$\text{At anode : }\ 2F^- -2e=F_2\ ;$$
$$\text{At cathode : }\ 2K^++2e=2K\ ;\ 2HF+2K=H_2+2KF$$

Thus, potassium is first liberated at the cathode ; this reacts with hydrogen fluoride reforming potassium fluoride and liberating hydrogen.

The apparatus in which the electrolysis is conducted consists of a U-tube made of platinum-iridium alloy. The U-tube is provided with two side tubes and fitted with fluorspar stoppers through which the electrodes made of the same alloy and thickened at the ends are inserted, the joints being made tight with lead washers and shellac. The solution of potassium fluoride in liquid hydrogen fluoride is taken in the U-tube and the whole apparatus is cooled by immersing it in a bath of boiling methyl chloride (b.pt., −23°C). Electric current is now passed through the solution when hydrogen is liberated at the cathode and fluorine at the anode.

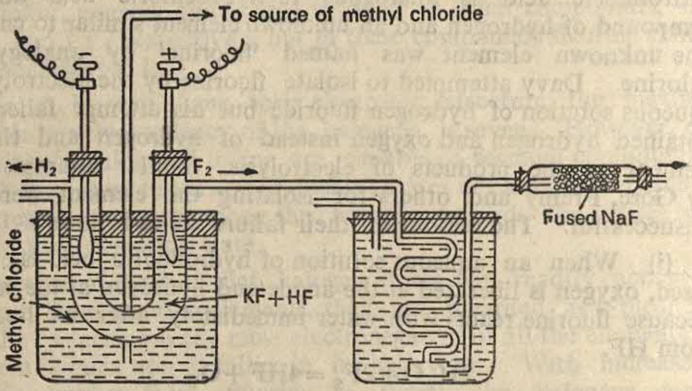

Fig. 10.1

Fluorine thus obtained is mixed with hydrofluoric acid vapour. In order to purify it, the gas is first passed through a platinum or copper spiral cooled in methyl chloride when most of hydrofluoric acid vapour condenses in the spiral and then through a tube of the same metal packed with fused sodium fluoride. Last traces of hydrofluoric acid vapours are absorbed by sodium fluoride forming sodium hydrogen fluoride.

$$NaF + HF = NaHF_2$$

Fluorine is then collected in a platinum jar by the upward displacement of air.

(ii) **Modern method.** Modern method of preparation of fiuorine is based on the electrolysis of fused potassium hydrogen fluoride. The apparatus used is shown in fig. 10.2.

It consists of a V-shaped copper vessel fitted with two side tubes for the escape of gases liberated at the electrodes. The ends of the vessel are closed by copper caps into which the graphite electrodes are fixed with bakelite cement. The vessel is filled with very pure and perfectly dry potassium hydrogen fluoride which is melted by passing an electric current through resistance wires wound around the copper vessel. Electric current is then passed through the molten electrolyte by means of graphite electrodes when hydrogen is evolved at the cathode and fluorine at the anode. The fluorine evolved is freed from the vapours of hydrogen fluoride by passing it through a copper U-tube packed with dry potassium fluoride which combines with hydrogen fluoride to form potassium hydrogen fluoride KHF_2. Fluorine is then collected in the platinum vessel by the upward displacement of air.

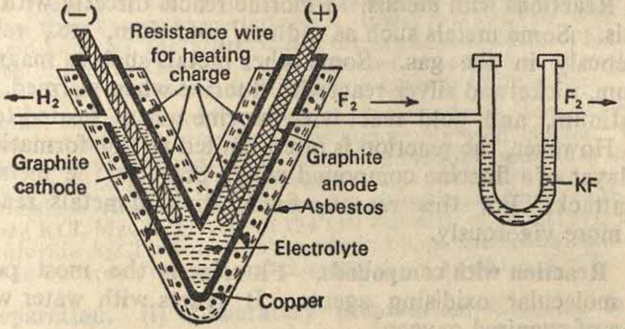

Fig. 10.2

The copper vessel is initially attacked by fluorine forming a layer of copper fluoride which protects the vessel from further attack.

Properties of fluorine. (A) **Physical properties :** Fluorine is a pale greenish yellow gas with a pungent odour. It condenses to a yellowish liquid at $-188°C$ and solidifies at $-218°C$. It is poisonous and has little action on glass. Free fluorine consists of diatomic molecules.

(B) **Chemical properties :** Chemically, fluorine is the most active of the elements. The extreme chemical activity of fluorine is due to its strong attraction for an electron necessary to fill up its outershell.

$$F + e = F^- + 82 \text{ kcal.}$$

(i) **Reaction with non-metals.** Fluorine reacts directly with all the non-metals except nitrogen, oxygen and inert gases. By indirect methods, its binary compounds with nitrogen and oxygen can be prepared. It combines with hydrogen with explosion even in the dark and at low temperatures forming hydrogen fluoride.

$$H_2 + F_2 = 2HF + 128 \text{ kcal.}$$

Sulphur, phosphorus, silicon, boron, carbon, bromine and iodine all ignite in the gaseous fluorine and burn with the formation of fluorides. The fluorides of non-metals are usually volatile and their formation does not protect the surface of the non-metals from the further action of fluorine. Hence, the reactions of non-metals with fluorine are often more vigorous than with many metals.

$$S+3F_2=SF_6 \; ; \; P_4+10F_2=4PF_5$$

$$C+2F_2=CF_4 \; ; \; 2B+3F_2=2BF_3$$

(ii) **Reactions with metals.** Fluorine reacts directly with nearly all metals. Some metals such as sodium, potassium, etc., take fire spontaneously in the gas. Some other metals such as magnesium, aluminium, nickel and silver react with fluorine when warmed. Metals like platinum, and gold react with fluorine when heated to about 300°C. However, the reaction is often limited to the formation of a surface layer of a fluorine compound which protects the metal from further attack. For this reason, finely divided metals react with fluorine more vigorously.

(iii) **Reaction with compounds.** Fluorine is the most powerful of the molecular oxidising agents. It reacts with water with the evolution of ozonised oxygen.

$$2F_2+2H_2O=O_2+4HF \; ; \; 3F_2+3H_2O=O_3+6HF$$

Fluorine when passed into aqueous solution of potassium chlorate $KClO_3$, oxidises it to potassium perchlorate, $KClO_4$. Hydrogen of many compounds is removed by fluorine to from hydrogen fluoride.

Fluorine displaces other halogens from their compounds, thus it liberates chlorine from sodium chloride and carbon tetrachloride.

$$2NaCl+F_2=2NaF+Cl_2$$

Fluorine reacts with dilute alkalis liberating fluorine monoxide but with concentrated alkalis, oxygen is evolved :

$$2NaOH+2F_2=2NaF+H_2O+F_2O$$

$$4NaOH+2F_2=4NaF+O_2+2H_2O$$

Organic substances such as alcohol, ether and turpentine take fire spontaneously in the gas.

Uses of fluorine. (a) Fluorine is used as an oxidising agent in some liquid rocket propellants. Some liquid propellant mixtures are (i) liquid hydrogen and fluorine, (ii) hydrazine, N_2H_4 and fluorine and (iii) ammonia NH_3 and fluorine.

(b) Fluorine is largely used for the fluorination of organic compounds, i.e., the substitution of fluorine for hydrogen. The fluoro-organic derivatives possess valuable properties.

(c) "Freon" CF_2Cl_2 a fluorine compound is a refrigerant. It is used in household refrigerators in place of ammonia or sulphur dioxide. Teflon, a polymeric fluorine compound, is used as an electric insulator.

(d) Large amount of fluorine is used for the conversion of uranium into uranium hexafluoride which is the only volatile compound of uranium. Uranium hexafluoride is used in the separation of the isotopes of uranium by the gaseous diffusion method.

Chlorine, Cl.

Chlorine was discovered by swedish chemist, K. W. Scheele, in 1774. He prepared the gas by the action of manganese dioxide on hydrochloric acid which was then known as *muriatic acid.* It was first belived to be an oxide of the acid and was, therefore, called the *oxymuriatic* acid. This view was disproved in 1810 by Davy who demonstrated conclusively the elementary nature of the gas and called it chlorine on account of its colour.

Chlorine, on account of its strong chemical activity, does not occur free in nature, but is found in combination commonly with metals. The most important among the naturally occurring metallic chlorides is sodium chloride or common salt which occurs in sea, in salt beds and in salt wells. The potassium chloride and magnesium chloride are found as the mineral *carnallite* ($KCl, MgCl_2, 6H_2O$) in the salt deposits of Stassfurt, Germany. Silver chloride AgCl is found as the mineral *horn silver.* Calcium chloride is found in nature as the mineral *chlorapatite*, $3Ca_3(PO_4)_2, CaCl_2$.

Preparation. (i) Laboratory preparation. Chlorine is usually prepared in the laboratory by the oxidation of hydrochloric acid. The oxidising agent which is most commonly used is manganese dioxide, MnO_2. Potassium permanganate, $KMnO_4$ bleaching powder $Ca(OCl)Cl$, or lead dioxide, PbO_2, may also be used as oxidant. The reaction between hydrochloric acid and manganese dioxide is represented by the equation :

$$MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O$$

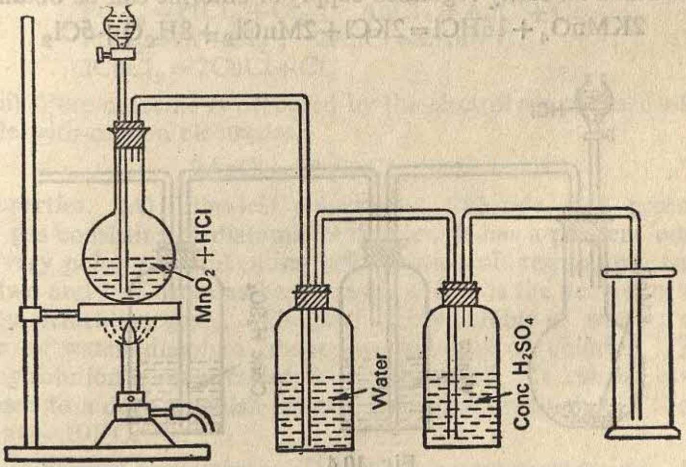

Fig. 10.3

The reaction takes place in two stages : at low temperatures, manganese trichloride, $MnCl_3$, is first formed as a dark brown solution, which decomposes on warming with the evolution of chlorine.

$$2MnO_2 + 8HCl = 2MnCl_3 + Cl_2 + 4H_2O$$
$$2MnCl_3 = 2MnCl_2 + Cl_2$$

Manganese dioxide is placed in a flask fitted with a thistle funnel and a delivery tube. Conc. hydrochloric acid is added through the thistle funnel in sufficient quantity so that it covers manganese dioxide and the end of the funnel dips into the acid. The mixture is then heated. Chlorine evolved is passed through a little water to remove hydrogen chloride and then through conc. H_2SO_4 to remove moisture. The dried gas is collected in gas jars by the upward displacement of air since chlorine is more dense than air it will settle at the bottom of the jar displacing the air upward. The gas cannot be collected by the displacement of cold water in which it is soluble or over mercury with which it reacts. It can, however, be collected over hot water or brine in which it is much less soluble.

Hydrochloric acid used in the above preparation may be obtained by heating a mixture of sodium chloride, and concentrated sulphuric acid. Hence, a mixture of sodium chloride, manganese dioxide and concentrated sulphuric acid may be used instead of hydrochloric acid and manganese dioxide.

$$2NaCl + 3H_2SO_4 + MnO_2 = 2NaHSO_4 + MnSO_4 + 2H_2O + Cl_2$$

(ii) **Preparation of chlorine at ordinary temperature.** Chlorine can be prepared by oxidising hydrochloric acid with potassium permanganate. The method is convenient since no external heat is required.and an easily regulated supply of chlorine can be obtained.

$$2KMnO_4 + 16HCl = 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$$

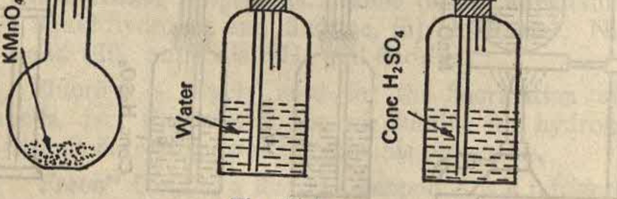

Fig. 10.4

Crystals of potassium permanganate are placed in a flask fitted with a dropping funnel and a delivery tube. Concentrated hydrochloric acid is then added drop by drop on the crystals through the dropping funnel. The reaction takes place in the cold ; chlorine evolved is passed through water to remove hydrogen chloride vapour and then through conc. H_2SO_4 to remove moisture.

The gas is collected by the upward displacement of air. By regulating the rate of flow of hydrochloric acid, the evolution of chlorine can be regulated.

(iii) Chlorine can be obtained by dropping cold concentrated hydrochloric acid on bleaching powder.

$$Ca(OCl)Cl+2HCl=CaCl_2+Cl_2+H_2O$$

(iv) Chlorine is also evolved when concentrated hydrochloric acid is heated with potassium dichromate.

$$K_2Cr_2O_7+14HCl=2KCl+2CrCl_3+7H_2O+3Cl_2$$

(v) Chlorine may also be obtained by heating hydrochloric acid with red lead or lead dioxide.

$$Pb_3O_4+8HCl=3PbCl_2+4H_2O+Cl_2$$
$$PbO_2+4HCl=PbCl_2+2H_2O+Cl_2$$

(vi) Chlorine can be prepared by passing a mixture of HCl and O_2 through a tube heated to 400°C and containing cupric chloride $CuCl_2$ as a catalyst, distributed over pieces of pumice.

$$4HCl+O_2\rightleftharpoons 2Cl_2+2H_2O$$

(vii) Chlorine can be prepared by decomposing the chlorides of gold, platinum and copper by heat.

$$PtCl_4=PtCl_2+Cl_2\ ;\quad AuCl_3=AuCl+Cl_2$$
$$PtCl_2=Pt+Cl_2\ ;\quad 2AuCl=2Au+Cl_2$$
$$2CuCl_2=2CuCl+Cl_2$$

(viii) Pure chlorine is prepared by the electrolysis of fused silver chloride with carbon electrodes.

$$2AgCl=2Ag+Cl_2$$

Properties. (A) Physical properties : Chlorine is a greenish yellow gas consisting of diatomic molecules. It has a pungent odour and is very poisonous and causes inflammation of respiratory tract. It is two and half times as heavy as air and so is the densest of the common elementary gases. The gas is fairly soluble in water ; one volume of water dissolves about two volumes of chlorine. The resulting solution is often called "chlorine water". It can be easily condensed to a dark greenish yellow liquid which boils at −34°C and freezes at −101°C.

(B) Chemical properties : Chlorine is a very reactive gas, but less reactive than fluorine. It reacts with most elements at room temperature or on gentle heating forming binary compounds called chlorides. In such compounds, the oxidation number of chlorine atom is usually −1.

(i) **Reaction with metals.** Chlorine combines directly with all metals to form metallic chlorides. However, the presence of moisture and/or the application of heat are often needed for the reaction to take place. Thus, sodium, copper, zinc, and iron react spontaneously with the moist chlorine but do not react with the dry gas at ordinary temperature.

$$2Na+Cl_2=2NaCl\ ;\ Zn+Cl_2=ZnCl_2$$

$$Cu+Cl_2=CuCl_2\ ;\ 2Fe+3Cl_2=2FeCl_3$$

Some finely powdered metals such as arsenic and antimony ignite spontaneously in the dry gas. When powdered antimony or arsenic are sprinkled into a jar of chlorine, they immediately ignite, and produce a shower of sparks.

$$2Sb+5Cl_2=2SbCl_5\ ;\ 2As+3Cl_2=2AsCl_3$$

The noble metals such as platinum and gold are attacked by chlorine when heated. The metal chlorides are ionic compounds.

$$2Au+3Cl_2=2AuCl_3$$

(ii) **Reaction with non-metals.** Chlorine combines directly with all of the non-metals except fluorine, oxygen, nitrogen, carbon and the inert gases. The chlorine compounds of carbon, oxygen or nitrogen can, however, be prepared by indirect methods. The chlorine compounds of non-metals are covalent.

(a) **Reaction with hydrogen.** Chlorine has a powerful affinity for hydrogen. The mixture of hydrogen and chlorine when exposed to diffused daylight combines slowly, but explodes violently in the direct sunlight. The combination is highly exothermic.

$$H_2+Cl_2=2HCl+44\text{ kcal.}$$

Hydrogen and chlorine combine rapidly and smoothly in presence of activated charcoal. This fact is utilised in the commercial production of hydrogen chloride. The following experiments illustrate the strong affinity of chlorine for hydrogen :

(i) A jet of hydrogen burning in air continues to burn with greenish flame when thrust into a jar of chlorine, with the production of hydrogen chloride.

(ii) A little turpentine $C_{10}H_{16}$ is heated in a test tube and then poured on a filter paper. The filter paper is then introduced into a jar of chlorine. The paper ignites spontaneously and continues to burn giving black clouds of carbon. A lighted candle also burns in chlorine with the liberation of carbon in the form of soots. Thus, chlorine combines only with hydrogen and not with carbon which is liberated in the form of black cloud.

$$C_{10}H_{16}+8Cl_2=16HCl+10C$$

(b) **Chlorine combines directly with sulphur, phosphorus and** boron forming their chlorides. When a piece of white phosphorus is inserted into a jar of chlorine, it ignites spontaneously.

$$2S+Cl_2=S_2Cl_2\ ;\ 2B+3Cl_2=2BCl_3\ ;\ P_4+6Cl_2=4PCl_3$$

(iii) **Reaction with compounds.** (a) **Reaction with water.** When chlorine is dissolved in water, hypochlorous acid and hydrochloric acid are formed through the interaction of chlorine and water.

$$Cl_2+H_2O\rightleftharpoons HOCl+HCl$$

If water saturated with chlorine gas is cooled to 0°C, yellow crystals of chlorine hydrate having the formula $Cl_2, 8H_2O$ separate out. When warmed, chlorine hydrate evolves about 100 times its volume of chlorine. This fact was utilised by Faraday in 1823 for the liquefaction of chlorine. Chlorine hydrate was taken in one limb of a bent tube (fig. 10.5) and the other limb was cooled by a freezing mixture. When the hydrate is warmed, chlorine is set free and condenses as a liquid in the cold limb. The gas pressure created by the vaporisation of the crystals is sufficient to liquefy chlorine at the temperature of the freezing mixture.

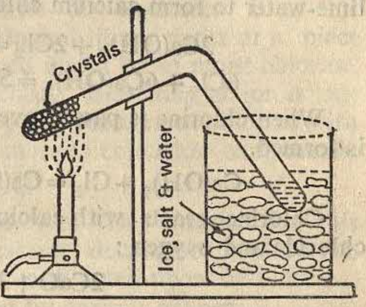

Fig. 10 5

If chlorine water is exposed to sunlight, the solution evolves oxygen. This is due to the decomposition of hypochlorous acid by light into hydrochloric acid and oxygen and to the reaction of activated chlorine with water.

$$2HOCl=2HCl+O_2\ ;\ 2Cl_2+2H_2O=4HCl+O_2$$

When steam and chlorine are passed through a heated tube, chlorine combines with hydrogen of steam forming hydrochloric acid liberating oxygen.

$$2H_2O+2Cl_2=4HCl+O_2$$

(b) **Reaction with alkali.** Chlorine reacts with cold, dilute solution of potassium, sodium or calcium hydroxide to give a mixture of chloride and hypochlorite of the metal.

$$\begin{array}{l} Cl_2+H_2O=HCl+HOCl \\ HCl+NaOH=NaCl+H_2O \\ HOCl+NaOH=NaOCl+H_2O \\ \hline Cl_2+2NaOH=NaCl+NaOCl+H_2O \end{array}$$

With excess of chlorine, a chloride and a chlorate are formed due to the decomposition of hypochlorite. Chlorine reacts with hot and concentrated alkali to yield a chloride and a chlorate. Hypochlorite which is first formed at the intermediate stage decomposes into chlorate and chloride ; thus

$$\begin{array}{l} 3Cl_2 + 6NaOH = 3NaCl + 3NaOCl + 3H_2O \\ \quad 3NaOCl = NaClO_3 + 2NaCl \\ \hline 3Cl_2 + 6NaOH = NaClO_3 + 5NaCl + 3H_2O \end{array}$$

Similarly, chlorine reacts with cold and dilute lime-water to form calcium chloride and calcium hypochlorite. It reacts with hot lime-water to form calcium chloride and calcium chlorate :

$$2Ca(OH)_2 + 2Cl_2 = CaCl_2 + Ca(OCl)_2 + 2H_2O$$

$$6Cl_2 + 6Ca(OH)_2 = 5CaCl_2 + Ca(ClO_3)_2 + 6H_2O$$

When chlorine is passed over dry slaked lime, bleaching powder is formed.

$$Ca(OH)_2 + Cl_2 = Ca(OCl)Cl + H_2O$$

Chlorine reacts with calcium oxide at red heat forming calcium chloride and oxygen :

$$2CaO + 2Cl_2 = 2CaCl_2 + O_2$$

(c) **Oxidising property of chlorine.** Chlorine is a strong oxidising agent because it is a powerful acceptor of electron. It oxidises sulphuretted hydrogen to sulphur, and liberates iodine from hydriodic acid. It readily displaces bromine and iodine from their compounds with metals.

$$H_2S + Cl_2 = 2HCl + S \; ; \; 2HI + Cl_2 = 2HCl + I_2$$

$$2KBr + Cl_2 = 2KCl + Br_2 \; ; \; 2KI + Cl_2 = 2KCl + I_2$$

It oxidises stannous salt to stannic salt and ferrous salt to ferric salt.

$$SnCl_2 + Cl_2 = SnCl_4 \; ; \; 2FeCl_2 + Cl_2 = 2FeCl_3$$

Chlorine reacts with ammonia forming nitrogen trichloride.

$$NH_3 + 3Cl_2 = NCl_3 + 3HCl.$$

But with excess of ammonia, chlorine forms nitrogen and ammonium chloride.

$$3Cl_2 + 8NH_3 = N_2 + 6NH_4Cl$$

Chlorine reacts with methane forming carbon tetrachloride and hydrochloric acid :

$$CH_4 + 4Cl_2 = 4HCl + CCl_4$$

In presence of water, chlorine oxidises sulphurous acid to sulphuric acid. In this type of reaction, chlorine first reacts with water producing nascent oxygen which then adds to the reducing agent, thus

$$\begin{array}{l} H_2O+Cl_2=2HCl+O \\ H_2SO_3+O=H_2SO_4 \\ \hline H_2O+Cl_2+H_2SO_3=2HCl+H_2SO_4 \end{array}$$

(d) Chlorine combines directly with many unsaturated compounds yielding addition compounds ; thus

$$CO+Cl_2=COCl_2 \text{ (phosgene)}$$

$$C_2H_4+Cl_2=C_2H_4Cl_2 \text{ (ethylene dichloride)}$$

(e) **Bleaching property of chlorine.** Chlorine bleaches many organic colouring matters in presence of moisture. If a few coloured flower petals or a piece of coloured litmus paper or a piece of cloth dyed with indigo is introduced into a jar of moist chlorine, then the colours are found to be bleached. Bleaching action is due to the nascent oxygen produced by the reaction of chlorine with water, which oxidises colouring substances to colourless compounds.

$$Cl_2+H_2O=2HCl+O$$

Hence, chlorine bleaches by oxididation. Dry chlorine for this reason cannot bleach. Chlorine cannot decolorise printer's ink because it contains carbon which is not acted upon by chlorine. Again, printer's ink remains unaffected by nascent oxygen.

Wet litmus paper when exposed to chlorine gas, first turns red and then becomes colourless. This is due to the fact that hypochlorous acid and hydrochloric acid which is first formed by the action of chlorine on water turns blue litmus red. Nascent oxygen which is subsequently formed by the decomposition of hypochlorous acid then decolourise the litmus by oxidation.

Uses of chlorine. (i) Large quantities of chlorine are used as bleaching agent in the manufacture of paper pulp and in the textile industry. Chlorine is too destructive to be used on fibres of animal origin such as wool, feather and silk. Chlorine is used in bleaching cellulose fabrics (linen and cotton) which are not damaged by it.

(ii) Chlorine is extensively used for the sterilisation of drinking water and water in swimming pools.

(iii) Chlorine is employed in the manufacture of dyes, drugs synthetic rubber, DDT (dichloro diphenyl trichloroethane) and non-inflammable solvents such as trichloroethylene. It is also used in the manufacture of bleaching powder, hydrochloric acid and important chlorides of silicon, carbon, sulphur phosphorus, arsenic, aluminium, tin and antimony.

(iv) It is used in the preparation of important drugs and explosives. It is used as a poison gas and for making the explosives such as phosgene, $COCl_2$, a lung irritant, mustard gas, and dichlorodiethyl sulphide which causes skin burns and blisters. Some organic phosphates containing a halogen atom are extremely toxic and inhibit the mechanism of nerve transmission.

(v) Chlorine finds employment in the extraction of gold and in degassing molten aluminium before casting.

Detection of chlorine. Chlorine is detected readily by its property of liberating iodine from potassium iodide. Free iodine gives blue colour with starch. Hence, when a piece of filter paper is dipped into a mixture of starch solution and potassium iodide and is then held over the gas, it gives blue colouration.

Bromine, Br

Bromine was discovered by A. J. Balard who prepared it in 1826 by chlorinating and then distilling the mother liquors of sea-water. The name "bromine" (from the greek *bromos*, stench) was applied by Balard because of its choking and unpleasant odour.

Bromine does not occur free in nature. In the combined state, small quantities of bromine occur in many silver ores. The principal sources of bromine are the waters of certain salt-water lake, and sea-water (0 007% Br on the average). Some quantities of bromine also occur as slight impurities in natural deposits of potassium salts and in oil-well brines. The content of bromine in the earth's crust is 3×10^{-5}%.

Preparation. (i) Bromine can be prepared by displacement from its salts by chlorine :

$$MgBr_2 + Cl_2 = Mg\ Cl_2 + Br_2$$

When chlorine is passed through a solution of potassium bromide, bromine is evolved.

$$2KBr + Cl_2 = 2KCl + Br_2$$

(ii) Laboratory preparation. In the laboratory, bromine is prepared by heating a mixture of potassium bromide, manganese dioxide and concentrated sulphuric acid.

$$2KBr + MnO_2 + 3H_2SO_4 = Br_2 + 2KHSO_4 + MnSO_4 + 2H_2O$$

A mixture of potassium bromide, manganese dioxide and concentrated sulphuric acid is taken in a stoppered glass retort, the end of which is introduced into a small flask immersed in cold water. The

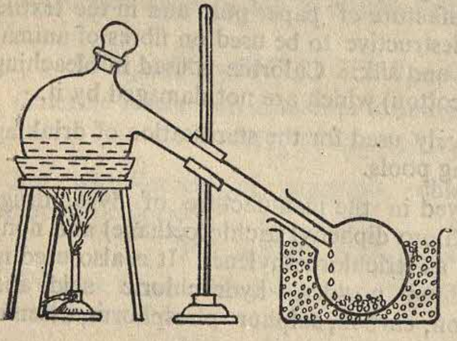

Fig. 10.6

retort is then carefully heated when bromine is liberated and distils over and condenses as dark brown liquid in the flask.

Manufacture of Bromine. The principal sources for the industrial production of bromine are (i) carnallite, KCl, $MgCl_2$, $6H_2O$ which contains about 0·3 per cent of bromine as magnesium bromide and (ii) sea-water which contains about 0·007% of bromine.

(i) **From carnallite.** Carnallite is first dissolved in water and the solution is concentrated by evaporation. On cooling the solution, potassium chloride separate out. The mother liquor (called *bittern*) left after the separation of potassium chloride contain magnesium chloride and magnesium bromide. The hot mother liquor is then allowed to flow slowly down a tower packed with pieces of porcelain and connected with a tank below. Steam and a current of chlorine are passed up the tower when chlorine reacts with bromide liquors flowing downwards, liberating bromine.

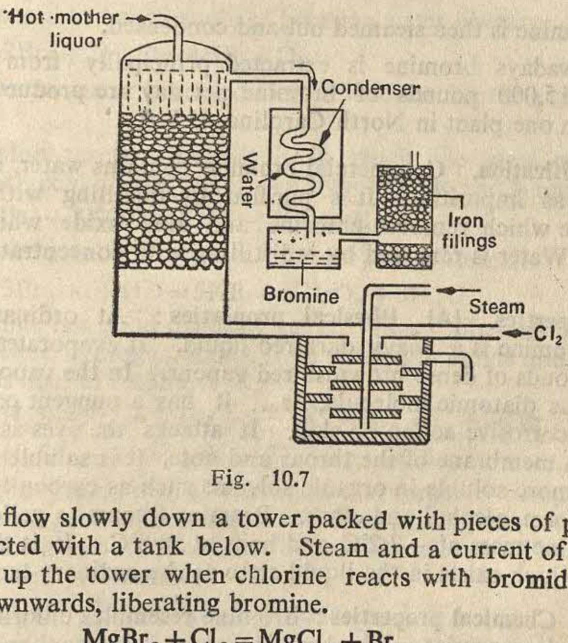

Fig. 10.7

$$MgBr_2 + Cl_2 = MgCl_2 + Br_2$$

The bromine thus liberated is converted by steam into vapour which escapes through an outlet at the top of the tower and condenses to a liquid into spiral tube cooled by water. Bromine vapours which escape condensation react with wet iron filings forming iron bromide.

Bromine in the waste liquor collected in the tank is recovered by passing steam through it when bromine is passed back again into the tower.

(ii) **From sea-water.** To extract bromine, sea-water is acidified with sulphuric acid (about 0·27 pound of 96% H_2SO_4 to each ton of sea-water) and then treated with chlorine when free bromine is liberated. Sulphuric acid is added in order to prevent the hydrolysis of bromine liberated owing to its high dilution.

$$Br_2 + H_2O \rightleftharpoons HBr + HOBr$$

The free bromine is then expelled from the very dilute solution by blowing air through it and absorbed in a solution of sodium carbonate in towers on the counter current principle.

$$3Na_2CO_3 + 3Br_2 = 5NaBr + NaBrO_3 + 3CO_2$$

The bromide-bromate mixture is acidified with sulphuric acid when free bromine is released.

$$5NaBr + NaBrO_3 + 3H_2SO_4 = 3Br_2 + 3Na_2SO_4 + 3H_2O$$

Bromine is then steamed out and condensed.

Nowadays bromine is extracted principally from sea-water. About 15,000 pounds of bromine per day are produced from sea-water in one plant in North Carolina, U.S.A.

Purification. Commercial bromine contains water, chlorine and iodine as impurities. It is purified by distilling with potassium bromide which removes chlorine and zinc oxide which removes iodine. Water is removed by redistilling with concentrated sulphuric acid.

Properties. (A) Physical properties : At ordinary temperature, bromine is a heavy dark-red liquid. It evaporates rapidly to form clouds of dense brownish red vapour. In the vapour state, it exists as diatomic molecule, Br_2. It has a pungent odour and a highly corrosive action on skin. It attacks the eyes as well as the mucous membrane of the throat and nose. It is soluble in water but much more soluble in organic solvents such as carbon tetrachloride, chloroform, alcohol and ether. Bromine freezes to yellowish brown crystalline mass at −7·2°C and boils at 58·8°C. It is the only non-metal which exists in the liquid state at the ordinary temperature.

(B) Chemical properties : Bromine resembles chlorine in general chemical properties. The bromine atom is larger than the chlorine atom and hence gains an electron less readily and holds into it less tightly than does the chlorine atom. Therefore, bromine reacts less vigorously than chlorine.

(a) Reaction with non-metals. Bromine does not react with hydrogen spontaneously, but reacts with it when heated, especially in the presence of platinised asbestos which acts as a catalyst.

$$H_2 + Br_2 = 2\ HBr$$

(b) It combines with sulphur, phosphorus and arsenic forming the corresponding bromides. It explodes in contact with white phosphorus forming tribromide PBr_3 and pentabromide PBr_5. It does not react with carbon, oxygen, or nitrogen.

$$3Br_2+2P=2PBr_3\ ;\ 5Br_2+2P=2PBr_5$$

(ii) **Reaction with metals.** Bromine reacts directly with active metals to form bromides. It explodes in contact with potassium but does not react with sodium in the cold.

$$2K+Br_2=2KBr$$

(iii) **Reaction with compounds.** (a) Bromine dissolves in water forming a red solution called bromine water, which contains some hypobromous acid HOBr and hydrobromic acid HBr.

$$Br_2+H_2O\rightleftharpoons HOBr+HBr$$

When exposed to bright sunlight bromine water liberates oxygen.

$$2Br_2+2H_2O=4HBr+O_2$$

When bromine water is cooled to 0°C, it forms bromine hydrate $Br_2, 8H_2O$.

(b) Bromine reacts with alkalis in much the same way as chlorine. With cold alkalis, it forms a hypobromite and a bromide.

$$Br_2+2KOH=KOBr+KBr+H_2O$$

But with hot alkalis, it yields a bromate and a bromide.

$$3Br_2+6KOH=5KBr+KBrO_3+3H_2O$$

(c) Bromine is a good oxidising agent. Thus it liberates sulphur from sulphuretted hydrogen, iodine from potassium iodide and oxidises sulphurous acid to sulphuric acids.

$$H_2S+Br_2=2HBr+S\ ;\ 2KI+Br_2=I_2+2KBr$$

$$H_2SO_3+H_2O+Br_2=H_2SO_4+2HBr$$

(d) Bromine reacts with a wide variety of organic compounds. With saturated organic compounds, it reacts replacing one or more hydrogen atoms by an equal number of bromine atoms. Thus, with ethane it forms ethyl bromide.

$$C_2H_6+Br_2=C_2H_5Br+HBr$$

With unsaturated organic compounds, it forms addition compounds.

$$\underset{\text{(ethylene)}}{C_2H_4}+Br_2=\underset{\text{(ethylene dibromide)}}{C_2H_4Br_2}$$

Uses of bromine. (i) The principal use of bromine is in the manufacture of tetraethyl lead, $(C_2H_5)_4Pb$, used as an antiknock compound in gasolines. The process consists of formation of ethyl bromide C_2H_5Br by the reaction between bromine and ethane, followed by the reaction between C_2H_5Br and an alloy of lead and sodium.

$$C_2H_6+Br_2=C_2H_5Br+HBr$$

$$4C_2H_5Br+4NaPb=(C_2H_5)_4Pb+4NaBr+3Pb$$

Ethylene dibromide $C_2H_4Br_2$ is added to the gasoline along with the tetraethyl lead. When the petrol is burnt in the presence of $C_2H_4Br_2$, lead is converted into volatile lead bromide $PbBr_2$ which is carried away in the hot exhaust gases in the form of lead bromide vapour ; in absence of the ethylene dibromide, lead is converted into non-volatile lead oxide which would remain to foul the engine cylinders.

(ii) Bromine is employed in the manufacture of dyes. In the laboratory, it is used as an oxidising agent and, for bromination of organic compounds.

(iii) Bromine is largely used in the manufacture of metal bromides such as those of sodium, potassium, calcium and strontium. They are used in medicines as nerve sedatives. Silver bromide is used in the manufacture of photographic films and papers.

Tests of bromine. Bromine is detected by its reddish-brown colour and pungent smell. If the gas is passed into water and the solution is shaken with carbon disulphide, then bromine if present is extracted by carbon disulphide which will be consequently-coloured brown.

Iodine

Iodine was first isolated from the ashes of burned sea-weeds in 1812 by the French chemist, Courtois. In 1813 Gay-Lussac established the elementary nature of iodine and showed that it was very similar to chlorine. The name iodine was given to the element because of the beautiful violet colour of its vapour (Gree *iodes* violet).

Iodine is never found free in nature. Sea-water contains very small quantity about 0·001 per cent of iodine. Sea-weeds and sponges absorb iodine from the sea-water and iodine can be manufactured from the ash of burnt sea-weeds to which the name *kelp* is given. An important technical source of iodine is the nitrate bed of chile which contains iodine in the form of sodium iodate, $NaIO_3$. Iodine is present in small quantities in the thyroid gland of animals.

(i) **Laboratory preparation of iodine.** In the laboratory, iodine is prepared by heating a mixture of potassium iodide, manganese dioxide and concentrated sulphuric acid.

$$2KI + MnO_2 + 3H_2SO_4 = MnSO_4 + 2KHSO_4 + I_2 + 2H_2O$$

A mixture of potassium iodide, manganese dioxide and cocentrated sulphuric acid is taken in a stoppered glass retort, the stem of which is introduced into the mouth of a small glass flask cooled by water. The retort is then heated when iodine is liberated ; the liberated iodine sublimes off and condenses into the flask in the form of shining black crystals.

(ii) Iodine is also liberated when chlorine or bromine is passed through concentrated solution of potassium iodide.

$$2KI + Cl_2 = 2KCl + I_2$$

(iii) **From sea-weeds.** The sea-weeds are dried and burnt. The ash from the burnt sea-weeds is called kelp which contains sodium and potassium iodides, chlorides, sulphates and carbonates and some magnesium salts. The kelp is heated with water and the solution is filtered. The filtrate is then concentrated when sodium and potassium chloride ; sodium and potassium sulphates and other impurities crystallise out whereas the more soluble sodium and potassium iodide remain in the mother liquor. The mother liquor is then mixed with manganese dioxide and sulphuric acid and distilled in cast-iron retorts. The liberated iodine sublimes off and the vapour condenses into a series of earthenware receivers called *aludels.*

$$2NaI+MnO_2+3H_2SO_4=2NaHSO_4+MnSO_4+2H_2O+I_2$$

(iv) **From crude chile saltpetre (caliche).** Chile saltpetre contains iodine in the form of sodium iodate. Sodium iodate remains in the mother liquor when sodium nitrate is crystallised from concentrated solution of the crude chile saltpetre. The mother liquor is then treated with a mixture of sodium sulphite and sodium bisulphite when iodine is precipitated.

$$2NaIO_3+3Na_2SO_3+2NaHSO_3=5Na_2SO_4+H_2O+I_2$$

The precipitate of iodine are collected and dried. It is purified by subliming with potassium iodide.

(v) **From oil-well brines.** The brine from certain oil-wells contains iodine in the form of iodides. Several different processes are used for the preparation of iodine from oil-well brines. All the processes involve the liberation of iodine from iodides by oxidation and subsequent collection of iodine.

In one process, brine is made just acidic with hydrochloric acid and is then mixed with sodium nitrite when iodine is liberated.

$$2NaI+2NaNO_2+4HCl=I_2+2NO+2H_2O+4NaCl$$

The solution is then stirred with activated charcoal when iodine is adsorbed on the charcoal. The charcoal is then filtered off and treated with hot sodium hydroxide solution when iodine is converted into sodium iodide and sodium iodate.

$$3I_2+6NaOH=5NaI+NaIO_3+3H_2O$$

The solution containing the mixture of iodate and iodide is concentrated and then acidified when iodine is precipitated.

$$NaIO_3+5NaI+6HCl=3I_2+6NaCl+3H_2O$$

In another process which is used more recently, brine is acidified with sulphuric acid and then a current of chlorine gas is passed through it. The liberated iodine is carried out by an air current and absorbed into a solution of hydriodic acid and sulphuric acid through which is passed sulphur dioxide. Sulphur dioxide reduces iodine to hydriodic acid.

$$I_2+SO_2+2H_2O=2HI+H_2SO_4$$

The mixture of hydriodic acid and sulphuric acid formed is then treated with chlorine when iodine is precipitated.

$$2HI+Cl_2=2HCl+I_2$$

Purification. Crude iodine may contain iodine chloride, ICl iodine bromide, IBr and iodine cyanide ICN all of which are volatile and hence cannot be removed by sublimation. It is mixed with potassium iodide and the mixture is heated when pure iodine sublimes. The impurities react with potassium iodide in the following manner.

$$ICl + KI = KCl + I_2$$

Properties. (A) **Physical properties.** Iodine forms grayish black crystals of semi-metallic lusture. The vapour pressure of iodine is very high at its melting point and hence it sublimes readily. The molecular formula of the vapour at temperatures below 700°C is I_2. It melts at 113°C and boils at 187°C. Iodine is slightly soluble in water but freely soluble into aqueous solution of potassium iodide due to the formation of potassium tri-iodide KI_3.

$$KI + I_2 \rightleftharpoons KI_3$$

Iodine is readily soluble in carbon disulphide, chloroform, benzene and other organic solvents. The colour of the solution becomes brown when the solvent contains oxygen atom in their molecules and the colour of the solution varies from pale pink to deep purple when the solvent contains no oxygen atom in their molecules. The brown colour is that of complex substances which is believed to be formed as a result of weak interaction between solvent and iodine molecules.

(B) **Chemical properties.** The reactions of iodine are analogous with those of other halogens although it is much less active chemically.

(i) **Reaction with non-metals.** Hydrogen and iodine unite at very high temperatures forming hydrogen iodide ; the reaction is reversible and is aided by the presence of a suitable catalyst.

$$H_2+I_2 \rightleftharpoons 2HI$$

Iodine burns in fluorine to form the pentafluoride, IF_5 which is a colourless liquid. It forms compounds with fluorine, chlorine and bromine, e.g., IF_7, ICl, ICl_3, IBr. It reacts with phosphorus forming the iodides PI_3 and P_2I_4. It does not combine directly with oxygen and sulphur.

$$2P+3I_2=2PI_3$$

(ii) **Reaction with metals.** Iodine reacts energetically with most metals forming iodides. Thus, antimony powder ignites spontaneously when it is shaken with iodine vapour.

$$2Sb + 3I_2 = 2SbI_3$$

When mercury is triturated with iodine, a green mercurous iodide, Hg_2I_2, is formed when mercury is in excess and a red mercuric iodide, HgI_2, is formed when iodine is in excess.

$$Hg + I_2 = HgI_2$$

(iii) **Reaction with compounds.** (a) Iodine reacts with cold dilute alkali forming iodide and hypoiodite.

$$I_2 + 2KOH \rightleftharpoons KI + KIO + H_2O$$

This reaction is reversible. The hypoiodite gradually changes into iodate and iodide even in the cold solution.

$$3KIO = KIO_3 + 2KI$$

Iodate is directly formed when iodine reacts with hot solution of alkali.

$$3I_2 + 6KOH = 5KI + KIO_3 + 3H_2O$$

(b) Iodine can act as an oxidising agent. Thus, it oxidises arsenite to arsenate, hydrogen sulphide to sulphur, sulphite to sulphate and stannous chloride to stannic chloride.

$$Na_3AsO_3 + I_2 + H_2O = Na_3AsO_4 + 2HI$$

$$H_2S + I_2 = 2HI + S$$

$$Na_2SO_3 + I_2 + H_2O = Na_2SO_4 + 2HI$$

$$SnCl_2 + I_2 + 2HCl = SnCl_4 + 2HI$$

Sodium thiosulphate is oxidised quantitatively to sodium tetrathionate ; this reaction is used in the estimation of iodine ;

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6$$

(c) Unlike other halogens, iodine is oxidised to iodic acid by concentrated nitric acid.

$$3I_2 + 10HNO_3 = 6HIO_3 + 10NO + 2H_2O$$

Uses. Iodine is used in medicine. The solution of iodine in alcohol called *tincture iodine* is used as disinfectant for wounds. It is used in the manufacture of dyes, drugs and iodoform CHI_3. In the laboratory, iodine finds employment in the synthesis of organic compounds and in volumetric analysis. Soluble iodides such as those of sodium and potassium are used in the treatment of simple goitre (enlargement of thyroid gland) which results from dietetic deficiency of iodine.

Tests of iodine. Iodine is detected by (i) its violet colour (ii) it forms intense blue colouration with starch solution (iii) it dissolves in carbon disulphide forming violet coloured solution.

(iv) it produces iodoform having sweet smell when treated with alcohol and sodium hydroxide.

Hydrogen fluoride, Hydrofluoric acid, HF.

Hydrogen and flourine combine instantly with explosion forming hydrogen fluoride. The solution of hydrogen fluoride in water is called hydrofluoric acid.

(i) **Preparation of hydrofluoric acid.** Hydrofluoric acid can be prepared by treating calcium fluoride with 90 per cent sulphuric acid at 120 to 300°C.

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF.$$

Powdered fluorspar is heated with 90 per cent sulphuric acid in a lead retort connected to a lead receiver which contains water. The hydrogen fluoride gas evolved passes into the receiver where it dissolves in water forming a colourless solution. Hydrofluoric acid thus obtained is stored in lead or gutta-percha or wax bottles because it attacks glass.

(ii) **Preparation of pure and anhydrous hydrofluoric acid.** Anhydrous hydrofluoric acid is prepared in the laboratory by heating potassium hydrogen fluoride which is known as Fremy's salt.

$$KHF_2 = KF + HF.$$

Pure and dry potassium hydrogen fluoride is heated in a platinum or copper retort connected with a condenser and a receiver of the same metal. The receiver is kept immersed in a freezing mixture. Potassium hydrogen fluoride decomposes evolving hydrogen fluoride which condenses in the receiver as a colourless liquid. The anhydrous acid thus obtained is stored in platinum or wax bottles.

(iii) Anhydrous hydrofluoric acid can also be prepared by heating lead fluoride in dry hydrogen or by passing dry hydrogen over dry silver fluoride.

$$PbF_2 + H_2 = Pb + 2HF$$

$$2AgF + H_2 = 2Ag + 2HF$$

Preparation of Fremy's salt. A known volume of aqueous hydrofluoric acid is neutralised with caustic potash. To the neutralised solution, a further equal volume of the same solution of hydrofluoric acid is added. The resulting liquid is evaporated in a platinum dish when crytstals of Fremy's salt, KHF_2 separate out. The crystals are then filtered off and dried by gentle heating.

$$HF + KOH = KF + H_2O, \ KF + HF = KHF_2$$

Properties. (A) Physical properties. Anhydrous hydrofluoric acid is a colourless, highly volatile liquid boiling at +19·5°C and freezing at −83°C. It is extremely soluble in water. It has pungent smell and fumes strongly in air. It vigorously attacks the walls of the respiratory tract and if inhaled may cause the permanent loss of voice. Anhydrous hydrofluoric acid is not an electrolyte but is an excellent ionising solvent. In aqueous solution, it behaves as a weak acid. Anhydrous hydrofluoric acid is highly associated because of the extreme electronegativity of the fluorine atom ; it withdraws electron from the hydrogen atom leaving essentially the positive proton to act as hydrogen bond. Anhydrous hydrofluoric acid is, therefore, formulated as (HF)n. The hydrogen bonds are formed according to the following scheme

$$\cdots H—F \cdots H—F \cdots H—F \cdots$$

(B) Chemical properties : (i) Reaction with metals. Hydrofluoric acid reacts with most metals (except gold, platinum, silver, mercury and lead) yielding metallic fluorides and hydrogen.

$$Fe + 2HF = FeF_2 + H_2$$

Hydrogen fluoride reacts with oxides of metals forming the metallic fluorides and water.

$$K_2O + 2HF = 2KF + H_2O$$

Many of the metallic fluorides have the property of combining with a further quantity of hydrogen fluoride to form the acid fluorides, thus,

$$KF + HF = KHF_2$$

(ii) Reaction with silica. Etching of glass. The outstanding property of hydrofluoric acid is its ability to react with sand, glass and other silicates, forming gaseous silicon tetrafluoride.

$$SiO_2 + 4HF = SiF_4 + 2H_2O$$

$$CaSiO_3 + 6HF = SiF_4 + CaF_2 + 3H_2O$$

The application of hydrofluoric acid for etching glass is based upon the reaction between HF and SiO_2. The glass is covered with a thin layer of wax. A design which is to be etched is scratched through the wax with stylus. The surface is then exposed to the action of hydrofluoric acid. The wax coating protects the unexposed glass. On removing wax by washing the glass with turpentine, the design is seen to be etched on the glass.

Etching may also be made with the hydrogen fluoride gas but the etching then appears opaque and dull. Etching made with the hydrofluoric acid is clear and shining.

Hydrofluoric acid attacks skin violently and forms burns which are painful and difficult to heal.

Fluorides. The salts of hydrofluoric acid are called fluorides. The fluorides are stable salts and in many ways resemble the chlorides. They differ from the chlorides in their ability of forming acid salts and complex salts. Thus, potassium fluoride forms the acid salt KHF_2 with hydrofluoric acid.

$$KF + HF = KHF_2$$

Acid ammonium fluoride is formed when normal ammonium fluoride is heated.

$$2NH_4F = NH_3 + NH_4HF_2$$

Silicon tetrafluoride reacts with water forming complex acid, e.g., silicofluoric acid.

$$3SiF_4 + 4H_2O = 2H_2SiF_6 + H_4SiO_4$$

From this acid, a series of complex salts called silicofluorides are derived, e.g., potassium silicofluoride, K_2SiF_6 and lead silicofluoride $PbSiF_6$. Potassium fluoride combines with boron trifluoride to form complex salt, potasium borofluoride.

$$KF + BF_3 = KBF_4$$

The solubilities of metallic fluorides often contrast sharply with those of other halides. Silver fluoride is readily soluble in water while the other halides of silver are only slightly soluble. Again, calcium fluoride is almost insoluble while other halides of calcium are soluble in water.

Uses of hydrofluoric acid and fluorides. (i) Hydrofluoric acid is used to etch various designs such as graduations on buret, and on glass. It is also used for the removal of sand from metal castings and in the chemical analysis of silicate minerals. Anhydrous hydrofluoric acid is employed as a catalyst in the production of high quality motor fuel and in other chemical processes. Large amounts of hydrogen fluoride are used for the production of cryolite which is employed in aluminium industry.

(ii) Certain fluorides find extensive practical applications. Thus sodium fluoride is used as an insecticide to destroy agricultural pests and as a preservant for impregnating wood. Many fluorides such as calcium fluoride are used as fluxes in metallurgical industry. They are also used as mordants in dye industry and in the synthesis of ceramics. Antimony trifluoride is used in the production of organic fluorine compounds.

Detection of hydrofluoric acid and fluoride. (i) The fluoride is mixed with sand and conc. H_2SO_4 and the mixture is heated in a leaden vessel. Conc. sulphuric acid reacts with the fluoride forming HF which instantaneously reacts with silica evolving vapours of SiF_4. A drop of water held by a platinum wire or by a glass rod into vapours becomes opalescent due to the formation of white insoluble silicic acid as a result of the reaction of SiF_4 with water.

$$CaF_2+H_2SO_4=CaSO_4+2HF\ ;\ 4HF+SiO_2=SiF_4+2H_2O$$

$$3SiF_4+4H_2O=2H_2SiF_6+\underset{\text{(silicic acid)}}{Si(OH)_4}$$

If free hydrofluoric acid is present, conc. H_2SO_4 is not added. (ii) when calcium chloride solution is added to a solution of a fluoride, a white precipitate of calcium fluoride insoluble in acetic acid is formed : $2NaF+CaCl_2=2NaCl+CaF_2$.

(iii) The free hydrofluoric acid is detected by its etching of glass.

Hydrogen chloride, Hydrochloric acid, HCl.

Hydrochloric acid was known to Arabian chemists of eighth century. In 1648, Glauber prepared the acid by the action of sulphuric acid on common salt. In 1772, Priestley collected the gas over mercury and found that it was very soluble in water. The solution was then called *muriatic acid*. When chlorine was recognised as an element, it was named hydrochloric acid.

Hydrogen chloride is found in gases evolved from some volcanoes. It is also present in animal and human gastric juice.

Preparation. Hydrogen chloride is a colourless gas and its solution in water is called hydrochloric acid. Hydrogen chloride can be prepared by the following methods :

(i) **By the direct union of hydrogen and chlorine.** When a mixture of hydrogen and chlorine is exposed to sunlight, they combine with an explosion, producing hydrogen chloride.

$$H_2+Cl_2=2HCl$$

(ii) **From chlorides of non-metals.** The chlorides of some non-metals react with water to yield hydrogen chloride.

$$PCl_3+3H_2O=H_3PO_3+3HCl$$

$$PCl_5+4H_2O=H_3PO_4+5HCl$$

$$SnCl_4+2H_2O=SnO_2+4HCl$$

These reactions are occasionally used for the preparation of hydrogen chloride in the laboratory.

The purest hydrogen chloride is prepared by the action of water on silicon tetrachloride.

$$SiCl_4+2H_2O=SiO_2+4HCl$$

(iii) **By the action of chlorine on steam.** Hydrogen chloride is also formed when a mixture of chlorine and steam is passed over heated active charcoal which acts as a catalyst.

$$2Cl_2+2H_2O=4HCl+O_2$$

(iv) **From sodium chloride. Laboratory preparation.** In the laboratory, hydrogen chloride is usually prepared by the action of concentrated sulphuric acid upon common salt. In the cold or on gentle heating, the following reaction takes place.

$$NaCl + H_2SO_4 = HCl + NaHSO_4 \qquad (10{\cdot}1)$$

But when the reaction mixture is heated to about 500°C, further reaction takes place.

$$NaHSO_4 + NaCl = Na_2SO_4 + HCl \qquad (10{\cdot}2)$$

Since the glass vessel must not be heated too strongly owing to the danger of cracking, the reaction (10·2) is not carried out in the laboratory.

Common salt is taken in a flask fitted with a thistle funnel and a delivery tube. Concentrated sulphuric acid is added through the thistle funnel and the mixture is warmed. Hydrogon chloride gas is evolved. The gas is then passed through a wash-bottle containing concentrated sulphuric acid which removes moisture. It is collected by upward displacement of air or over mercury. It cannot be collected by the displacement of water as it is highly soluble in water. Hydrogen chloride cannot be dried over phosphorus pentoxide because it reacts according to the equation.

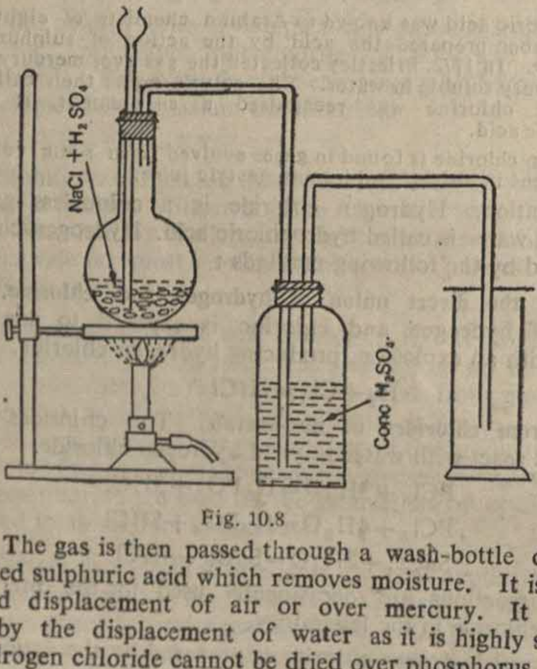

Fig. 10.8

$$2P_2O_5 + 3HCl = POCl_3 + 3HPO_3$$

The strengths of sulphuric acid, hydrochloric acid and nitric acid are in the order: $H_2SO_4 > HCl > HNO_3$. Among these acids sulphuric acid is least volatile. Hence, the volatile hydrochloric acid is displaced by less volatile and stronger sulphuric acid.

Preparation of aqueous solution of hydrogen chloride. In order to prepare the aqueous solution of hydrogen chloride, the end of the delivery tube is connected with the stem of an inverted funnel which dips just below the surface of water contained in a beaker. Hydrogen chloride dissolves in water, yielding an aqueous solution of hydrogen chloride or hydrochloric acid.

Owing to the high solubility of the gas in water, reduction of pressure inside the flask may take place. As a result, water is drawn up into the funnel and water level in the beaker falls; consequently, air passes into the funnel and the water falls back into the beaker. This device prevents water in the beaker from being sucked back up the delivery tube on to the hot sulphuric acid in the flask, and is known as anti-suction device.

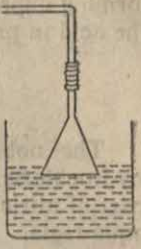

Fig. 10.9

Properties. (A) Physical properties. Hydrogen chloride is a colourless gas with a pungent, suffocating smell. It attacks the mucous membrane of the nose and throat. It is denser than air. Hydrogen chloride can easily be condensed to a liquid which boils at −85°C and freezes at −114·8°C. Liquid hydrogen chloride is not a conductor of electricity.

The gas is extremely soluble in water; its concentrated solution fumes strongly in moist air due to the liberation of hydrogen chloride. Ordinary concentrated hydrochloric acid contains about 37 per cent HCl and has a specific gravity of 1·19.

When concentrated hydrochloric acid is heated, hydrogen chloride escapes first and the solution gets diluted. This continues until the solution contains 20·2 per cent of HCl. This solution distils without change of composition, at a constant temperature of 110°C. On the other hand, when dilute hydrochloric acid is boiled, water escapes first and the solution becomes concentrated. This continues until the solution contains 20·2 per cent HCl. The solution distils without altering its composition at the constant temperature of 110°C. The 20·2 per cent solution of hydrochloric acid is called a constant boiling solution or a constant boiling mixture.

(B) Chemical properties: (i) **Reaction with metals.** The molecules of hydrogen chloride when dissolved in water appear to be completely dissociated into H^+ and Cl^- ions.

$$HCl \rightleftharpoons H^+ + Cl^-$$

Therefore, in aqueous solution hydrogen chloride behaves as a strong mono-basic acid. It reacts readily with many metals liberating hydrogen and forming salts, known as metal chlorides, thus

$$Zn + 2HCl = ZnCl_2 + H_2$$

$$Fe + 2HCl = FeCl_2 + H_2$$

$$Sn + 2HCl = SnCl_2 + H_2$$

Copper dissolves slowly in concentrated hydrochloric acid, forming cuprous chloride and hydrogen. Silver slowly reacts with the acid in presence of air.

$$2Cu+4HCl=H_2+2HCuCl_2$$
$$4Ag+4HCl+O_2=4AgCl+2H_2O$$

The noble metals such as platinum and gold do not dissolve in hydrochloric acid, but they dissolve readily into a mixture of one part of nitric acid and three parts of hydrochloric acid, known as aqua regia.

$$3HCl+HNO_3=Cl_2+2H_2O+NOCl \text{ (nitrosyl chloride)}$$
$$Au+4HCl+HNO_3=NO+2H_2O+HAuCl_4 \text{ (aurichloric acid)}$$

(ii) **Reaction with non-metals.** Hydrogen chloride neither burns nor is a supporter of combustion. It reacts with free oxygen only under the influence of catalysts such as cupric salts.

$$4HCl+O_2=2H_2O+2Cl_2$$

Fluorine displaces chlorine from HCl forming hydrofluoric acid.

$$2HCl+F_2=2HF+Cl_2$$

(iii) **Reaction with compounds.** (a) **Reaction with bases.** In presence of traces of moisture, hydrogen chloride reacts readily with ammonia, forming ammonium chloride.

$$NH_3+HCl=NH_4Cl$$

Hydrochloric acid reacts readily with the hydroxides of the metals forming metallic chlorides and water.

$$Ca(OH)_2+2HCl=CaCl_2+2H_2O$$
$$NaOH+HCl=NaCl+H_2O$$
$$Al(OH)_3+3HCl=AlCl_3+3H_2O$$

These metathetical reactions are known as neutralisation reactions. The acid reacts with carbonates, bicarbonates, sulphites and oxides of metals forming metal chlorides and other characteristic products.

$$\begin{array}{ll} CaCO_3+2HCl & =CaCl_2+H_2CO_3 \text{ (carbonic acid)} \\ H_2CO_3 & =H_2O+CO_2 \\ \hline CaCO_3+2HCl & =CaCl_2+H_2O+CO_2 \end{array}$$
$$Na_2CO_3+2HCl=2NaCl+H_2O+CO_2$$
$$NaHCO_3+HCl=NaCl+H_2O+CO_2$$
$$CuO+2HCl=CuCl_2+H_2O$$
$$Na_2SO_3+2HCl=2NaCl+H_2O+SO_2$$

(b) Reaction with oxidising agents. Oxidising agents such as manganese dioxide, lead dioxide, potassium permanganate, potassium dichromate, etc., oxidise hydrochloric acid to chlorine.

$$4HCl+MnO_2=MnCl_2+Cl_2+2H_2O$$

$$K_2Cr_2O_7+14HCl=2KCl+2CrCl_3+7H_2O+3Cl_2$$

$$2KMnO_4+16HCl=2KCl+2MnCl_2+5Cl_2+8H_2O$$

Uses of hydrochloric acid. (i) Hydrochloric acid is employed for purifying iron ores, coke and clay. It also finds applications in dyestuff, leather and food industry. It is used for the preparation of glue, and a number of organic preparations. A small amount of hydrochloric acid is present in gastric juices of man and animal and plays an important part in digestion. (ii) It is used for "pickling" sheet iron in galvanising and tinplate industries. It is used as an analytical reagent in chemical industry. (iii) Aqua regia which is a mixture of three parts of hydrochloric acid and one part of nitric acid is used for dissolving gold to form gold chloride which is an important photographic chemical.

(iv) Hydrochloric acid is used for preparing metal chlorides, many of which find wide applications. For Example, sodium chloride is a necessary seasoning for our food. Potassium chloride is used as an important fertiliser. Calcium chloride $CaCl_2, 6H_2O$ is used for preparing 'cooling mixture". Anhydrous calcium chloride is used as a drying agent in the laboratory. Mercuric chloride, $HgCl_2$, is used to preserve wood and anatomical preparations. Very dilute solution of mercuric chloride (1 : 1000) is an efficient disinfectant.

Tests. (i) When hydrochloric acid or any metallic chloride is heated with manganese dioxide and concentrated sulphuric acid, greenish yellow gas chlorine is evolved.

(ii) When silver nitrate solution is added to the solution of a chloride or hydrochloric acid, white precipitates of silver chloride are obtained. This precipitate is insoluble in dil. nitric acid but soluble in *ammonium hydroxide.*

$$HCl+AgNO_3=AgCl+HNO_3$$

$$AgCl+2NH_4OH=[Ag(NH_3)_2]Cl+2H_2O$$

$$[Ag(NH_3)_2]Cl+2HNO_3=AgCl+2NH_4NO_3$$

Hydrogen bromide, Hydrobromic acid, HBr

Preparation. (i) **By synthesis.** Hydrogen bromide can be prepared by the direct combination of hydrogen and bromine. When a mixture of hydrogen and bromine vapour is passed through a tube containing a red-hot spiral of platinum wire, gaseous hydrogen bromide is formed.

$$H_2+Br_2=2HBr$$

This method is used for the preparation of anhydrous gas on a large scale.

A mixture of hydrogen and bromine obtained by passing dry hydrogen through bromine kept in a wash-bottle heated to about 50°C by a bath of hot water is passed through a tube containing red-hot spiral of platinum wire. Hydrogen combines with bromine in the tube ; the platinum wire acts as a catalyst. The hydrogen bromide formed is then passed over moist red phosphorus which converts free bromine into hydrobromic acid. The gas is then dried by passing it over fused calcium bromide and finally cooled air when anhydrous hydrogen bromide solidifies and unreacted hydrogen passes out.

(ii) Hydrogen bromide can be conveniently prepared by the action of hydrogen sulphide on bromine or by the action of sulphur dioxide on bromine in presence of a little water.

$$Br_2 + H_2S = 2HBr + S$$

$$Br_2 + 2H_2O + SO_2 = 2HBr + H_2SO_4$$

A stream of hydrogen sulphide or sulphur dioxide is passed through bromine mixed with a little water in a wash-bottle(fig. 10.10).

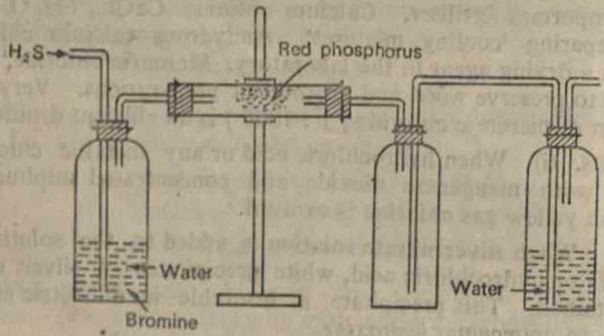

Fig. 10.10

Hydrogen bromide formed is then allowed to pass through a tube containing moist red phosphorus which removes uncombined bromine. The gas is then collected by the upward displacement of air or over mercury. The gas may be dissolved in water by an arrangement shown in fig. 10.10.

(iii) **From metallic bromides.** Hydrogen fluoride and hydrogen chloride can be prepared by the reaction between concentrated sulphuric acid and a metal fluoride and chloride respectively. But hydrogen bromide and hydrogen iodide cannot be prepared by the action of concentrated sulphuric acid on a metallic bromide or metallic iodide because the halides HF, HCl, HBr, and HI are increasingly stronger reducing agents while concentrated sulphuric acid is an oxidant. Hydrogen bromide and hydrogen iodide are sufficiently strong reducing agents to reduce the sulphuric acid whereas they are oxidised by sulphuric acid to bromine and iodine respectively. Thus :

$$2KBr + 2H_2SO_4 = 2KHSO_4 + 2HBr$$
$$2HBr + H_2SO_4 = Br_2 + 2H_2O + SO_2$$

$$2KBr + 3H_2SO_4 = 2KHSO_4 + Br_2 + 2H_2O + SO_2$$

Similarly,

$$2KI + 3H_2SO_4 = 2KHSO_4 + I_2 + 2H_2O + SO_2$$

Therefore, sulphuric acid cannot be used to prepare hydrogen bromide and hydrogen iodide. Instead non-oxidising and high boiling-point acid such as orthophosphoric acid is used.

$$NaBr + H_3PO_4 = NaH_2PO_4 + HBr$$

The hydrogen bromide may be removed by heating the reaction mixture to drive off gaseous HBr which may be collected over mercury or by the upward displacement of air.

This method is not carried out in the laboratory but it is customary instead to prepare hydrogen bromide in the laboratory by the hydrolysis of phosphorus tribromide, PBr_3.

(iv) **Laboratory preparation of hydrogen bromide.** In the laboratory, hydrogen bromide is prepared by the action of bromine on red phosphorus in the presence of water. Phosphorus tribromide and pentabromide are first formed ; they are then hydrolysed by water forming hydrogen bromide and phosphorous and phosphoric acid respectively :

$$2P + 3Br_2 = 2PBr_3 \text{ ; } PBr_3 + 3H_2O = H_3PO_3 + 3HBr$$
$$2P + 5Br_2 = 2PBr_5 \text{ ; } PBr_5 + 4H_2O = H_3PO_4 + 5HBr$$

A mixture of red phosphorus with twice its weight of water and some clean sand are taken in a flask equipped with a dropping funnel and an outlet tube (fig. 10.11). The outlet tube is connected to the two U-tubes ; one containing pieces of glass smeared with damp red phosphorus and the other containing granules of anhydrous calcium bromide. The bromine is allowed to drop slowly into the red phosphorus from the dropping funnel when a vigorous reaction takes place with the evolution of much heat. Hydrogen bromide given off passes first through the U-tube containing damp red phosphorus which removes any unchanged bromine and then through the U-tube containing anhydrous calcium bromide which removes moisture. The gas is finally collected by the upward displacement of air.

In order to prepare the aqueous solution of hydrogen bromide, the U-tube containing damp red phosphorus is connected with the stem of the funnel which dips just below the surface of water contained in a beaker. Hydrogen bromide dissolves in water giving hydrobromic acid.

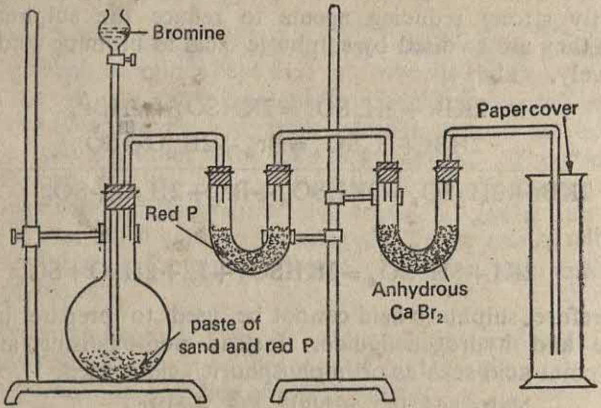

Fig. 10.11

Properties. (A) **Physical properties** : Hydrogen bromide is a colourless gas having pungent odour. It is heavier than air and fumes strongly in moist air. The gas condenses to a liquid at −67°C and solidifies to a colourless solid at −86°C. The gas is very soluble in water. On distillation of the aqueous solution, a mixture of constant boiling is obtained, which contains 48% hydrobromic acid and boils at 125°C. Dry hydrogen bromide has no action on litmus paper.

(B) **Chemical properties** : In most of its chemical properties, hydrogen bromide resembles hydrogen chloride. Hydrogen bromide is less stable than hydrogen chloride and dissociates slightly into hydrogen and bromine when heated to about 800°C. Slight decomposition also occurs when the gas is exposed to sunlight.

$$2HBr \rightleftharpoons H_2+Br_2$$

(i) **Reaction with non-metals.** Hydrogen bromide is oxidised more readily than hydrogen chloride. Thus, it is oxidised by air in the presence of sunlight.

$$4HBr+O_2=2H_2O+2Br_2$$

It readily reacts with chlorine forming hydrochloric acid and bromine.

$$2HBr+Cl_2=2HCl+Br_2$$

(ii) **Reaction with metals.** Aqueous hydrobromic acid reacts with metals with the evolution of hydrogen. It reacts with mercury very slowly forming mercury bromide and hydrogen. Potassium readily displaces hydrogen from HBr and form potassium bromide.

$$2HBr + 2K = H_2 + 2KBr$$

(iii) **Reaction with compounds.** Hydrobromic acid reacts with oxides, hydroxides and carbonates of the metal in the same way as hydrochloric acid to form bromides. It is more readily oxidised than hydrochloric acid ; thus it is oxidised by sulphuric acid and hydrogen peroxide to bromine ; but hydrochloric acid is not oxidised by either of these.

$$2HBr + H_2SO_4 = Br_2 + SO_2 + 2H_2O$$

$$2HBr + H_2O_2 = Br_2 + 2H_2O$$

Like hydrochloric acid, it is oxidised by manganese dioxide, potassium permanganate, etc., to bromine.

Uses. Hydrobromic acid is used as a laboratory reagent and in medicine.

Tests of HBr and Bromides. (i) When silver nitrate solution is added to a solution of hydrobromic acid or a bromide acidified with HNO_3, a pale yellow precipitate of silver bromide is formed :

$$KBr + AgNO_3 = KNO_3 + AgBr \text{ ; } HBr + AgNO_3 = HNO_3 + AgBr$$

Silver bromide is insoluble in nitric acid but moderately soluble in ammonia solution.

(ii) To a solution of HBr or a bromide in a test tube, a few c.c. of chloroform and a little chlorine-water are added. Bromine is liberated and on shaking it passes into the chloroform layer colouring it brown.

(iii) When HBr or a bromide is heated with concentrated H_2SO_4, red vapours of bromine are evolved.

Hydrogen iodide, Hydriodic acid, HI

Preparation. (i) **By synthesis.** Hydrogen iodide can be prepared by the direct union of hydrogen and iodine. When hydrogen and iodine vapour are passed through a tube containing heated platinised asbestos, hydrogen iodide is formed.

$$H_2 + I_2 \rightleftharpoons 2HI$$

This method is utilised for the commercial preparation of hydrogen iodide by carrying out the reaction at about 200°C, under pressures of 12-15 atmospheres and in the presence of a chromium trioxide catalyst.

(ii) An aqueous solution of hydrogen iodide (hydriodic acid) can be prepared by passing hydrogen sulphide slowly through a suspension of iodine in water until the colour of iodine has disappeared. Hydrogen sulphide reacts with iodine forming hydriodic acid and precipitating sulphur.

$$H_2S+I_2=2HI+S$$

Excess of hydrogen sulphide is removed by passing a stream of carbon dioxide or hydrogen through the solution. The precipitated sulphur is then filtered off and the filtrate is a solution of hydrogen iodide in water. It can be concentrated to about 57 per cent by distillation.

(iii) Hydrogen iodide cannot be prepared by the action of concentrated sulphuric acid on metallic iodides since hydrogen iodide formed reduces sulphuric acid to sulphur dioxide.

$$\begin{array}{c} 2KI+2H_2SO_4=2KHSO_4+2HI \\ 2HI+H_2SO_4=SO_2+I_2+2H_2O \\ \hline 2KI+3H_2SO_4=2KHSO_4+SO_2+I_2+2H_2O \end{array}$$

The gas can be prepared by the action of phosphoric acid on potassium iodide.

$$3KI+H_3PO_4=3HI+K_3PO_4$$

(iv) **Laboratory preparation.** In the laboratory, hydrogen iodide is prepared by the action of water on a mixture of red phosphorus and iodine. Phosphorus tri-iodide is first formed and this is hydrolysed by water forming hydriodic acid.

$$\begin{array}{c} 2P+3I_2=2PI_3 \\ 2PI_3+6H_2O=2H_3PO_3+6HI \\ \hline 2P+3I_2+6H_2O=2H_3PO_3+6HI \end{array}$$

A mixture of red phosphorus and iodine is taken into a flask fitted with a dropping funnel and an outlet tube. Water is then allowed to fall drop by drop from the dropping funnel onto the mixture. Hydrogen iodide is evolved and is passed through a U-tube containing moist red phosphorus which removes free iodine. The gas is then collected by the upward displacement of air. It cannot be collected over mercury since mercury and hydrogen iodide react.

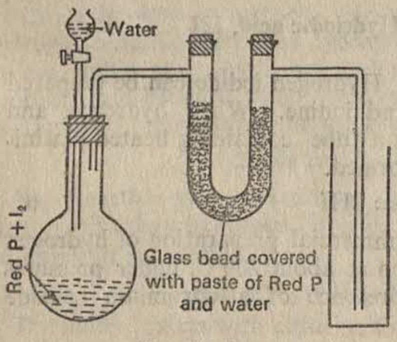

Fig. 10.12

An aqueous solution of the gas can be prepared by leading hydrogen iodide into water in a way similar to that adopted in the case of hydrogen chloride.

Properties. (A) **Physical properties.** Pure hydrogen iodide is a colourless gas which fumes strongly in air. It has an irritating odour and is heavier than air. It may be condensed to a colourless anhydrous liquid which freezes at −50·7°C and boils at −35·4°C. It is highly soluble in water and like other hydrogen halide it forms constant boiling mixture which boils at 127°C under standard pressure. The constant boiling mixture contains 57% of hydrogen iodide.

(B) **Chemical properties :** (i) Hydrogen iodide is decomposed by heat or when exposed to sunlight into hydrogen and iodine.

$$2HI = H_2 + I_2$$

The aqueous solution of hydrogen iodide (hydriodic acid) is strongly acidic, because in aqueous solution it ionises completely :

$$HI \rightleftharpoons H^+ + I^-$$

It reacts with bases forming salts known as iodides.

(i) It is a powerful reducing agent. All common oxidising agents, therefore, liberate iodine from hydriodic acid. Thus, when fresh solution of the acid which is colourless is exposed to air, it rapidly becomes brown due to the oxidation by air.

$$4HI + O_2 = 2I_2 + 2H_2O$$

It reduces ferric chloride to ferrous chloride, chlorine to hydrochloric acid, bromine to hydrobromic acid, hydrogen peroxide to water, nitric acid to nitrogen dioxide and sulphuric acid to sulphur dioxide. In all cases, it is oxidised to iodine.

$$2FeCl_3 + 2HI = 2FeCl_2 + I_2 + 2HCl$$

$$2HI + Cl_2 = 2HCl + I_2$$

$$2HI + Br_2 = 2HBr + I_2$$

$$2HI + H_2O_2 = 2H_2O + I_2$$

$$2HNO_3 + 2HI = 2H_2O + I_2 + 2NO_2$$

$$H_2SO_4 + 2HI = SO_2 + I_2 + 2H_2O$$

$$H_2O_2 + 2HI = 2H_2O + I_2$$

Hydrogen iodide is oxidised by ozone to iodine.

$$2HI + O_3 = H_2O + O_2 + I_2$$

When hydriodic acid is added to acidified solution of potassium permanganate, it is oxidised to iodine.

$$2KMnO_4 + 4H_2SO_4 + 10HI = 2MnSO_4 + 2KHSO_4 + 8H_2O + 5I_2$$

Hydriodic acid is oxidised by acidified solution of potassium dichromate to iodine.

$$K_2Cr_2O_7 + 5H_2SO_4 + 6HI = Cr_2(SO_4)_3 + 2KHSO_4 + 7H_2O + 3I_2$$

Hydrogen iodide is oxidised by nitric acid to iodine.

$$2HNO_3+2HI=2H_2O+I_2+2NO_2$$

Nitrous acid is reduced to nitric oxide by hydrogen iodide.

$$2HNO_2+2HI=2H_2O+2NO+I_2$$

Mild reducing agents such as copper sulphate, and ferric chloride oxidise hydriodic acid to iodine.

$$2CuSO_4+4HI=Cu_2I_2+2H_2SO_4+I_2$$

$$2FeCl_3+2HI=2FeCl_2+I_2+2HCl$$

Incidentally, it may be mentioned that the mild oxidising agents such as $FeCl_3$ and $CuSO_4$ cannot oxidise hydrobromic acid to bromine but they can oxidise hydriodic acid to iodine. This shows that hydriodic acid is a stronger reducing agent than hydrobromic acid.

Uses. Hydriodic acid is used as reducing agent in organic chemistry.

Tests. Hydriodic acid and iodides are detected by the following tests :

(i) When hydriodic acid or metallic iodides are heated with concentrated sulphuric acid, violet vapours of iodine are evolved.

(ii) On adding silver nitrate solution to a solution of hydrogen iodide or metallic iodide acidified with nitric acid, yellow precipitates of silver iodide are formed.

$$HI+AgNO_3=AgI+HNO_3$$

(iii) On shaking a solution of hydrogen iodide or a metallic iodide with carbon disulphide and chlorine-water, carbon disulphide layer turns violet.

$$2HI+Cl_2=2HCl+I_2$$

Chlorine liberates, from hydriodic acid or metallic iodide, iodine which dissolves in carbon disulphide giving a violet solution.

Comparative study of fluorine, chlorine, bromine and iodine. There are similarities in properties among fluorine, chlorine, bromine and iodine. These elements display a remarkable gradation in their physical and chemical properties with increase in atomic weights. Except fluorine, all other halogen elements can be prepared in the laboratory by the general method.

$$2NaX+MnO_2+3H_2SO_4=2NaHSO_4+MnSO_4+X_2+2H_2O$$

(X = Cl, Br and I)

Fluorine is prepared by the electrolysis of a solution of potassium fluoride in liquid hydrogen fluoride.

The intensity of colour, melting points and boiling points of these elements increase with increase in atomic weights. Their chemical properties also change with increasing atomic weights. The order of activity is fluorine, chlorine, bromine and iodine; fluorine is most reactive and displays an unparallel readiness to enter into chemical combination with other elements. It liberates chlorine, bromine and iodine from their hydracids and salts.

$$2KCl+F_2=2KF+Cl_2\ ;\ 2KBr+F_2=2KF+Br_2$$
$$2KI+F_2=2KF+I_2$$

Chlorine is less reactive than fluorine but more reactive than bromine and iodine. It displaces bromine and iodine from their hydracids and salts.

$$2KBr+Cl_2=2KCl+Br_2\ ;\ 2KI+Cl_2=2KCl+I_2$$

Bromine is more reactive than iodine. Hence, it displaces iodine from its hydracid and salt.

$$2KI+Br_2=2KBr+I_2$$

Reaction with hydrogen. All these elements react with hydrogen to form their hydracids.

$$H_2+X_2=2HX\ (\ X=F,\ Cl,\ Br\ \text{and}\ I\ )$$

The rate of the reaction decreases from fluorine to iodine. Fluorine explosively reacts with hydrogen even at the low temperature to form hydrogen fluoride. Chlorine does not react with hydrogen in the dark but the reaction takes place in the presence of sunlight with the formation of hydrogen chloride. Bromine reacts with hydrogen only when heated forming hydrogen bromide. Iodine reacts with hydrogen in the presence of heated catalyst forming hydrogen iodide.

Reaction with non-metals. Fluorine directly combines with all non-metals except oxygen and nitrogen. Chlorine combines directly with all non-metals except oxygen, nitrogen and carbon. Excepting oxygen, nitrogen, carbon and silicon, bromine combines directly with all other non-metals. Iodine combines only with phosphorus, arsenic and other halogen elements.

Reaction with metals. Fluorine reacts with all metals. Almost all metals are attacked by chlorine. Majority of the metals react with bromine. Iodine reacts with most of the metals.

Reaction with water. At ordinary temperature, fluorine violently reacts with water forming hydrogen fluoride and ozonised oxygen. Chlorine and bromine reacts with water in the presence of sunlight. Iodine does not react with water.

$$2X_2+2H_2O=4HX+O_2\ (\ X=F,\ Cl\ \text{and}\ Br\ )$$

Reaction with alkalis. Fluorine reacts with alkali solution forming fluoride and F_2O. With cold and dilute alkali solution, chlorine forms chloride and hypochlorite, and bromine forms bromide and hypobromite. With hot and concentrated alkali solution chlorine forms chloride and chlorate and bromine forms bromide and bromate.

$$2F_2+2NaOH=2NaF+H_2O+F_2O$$
$$X_2+2NaOH=NaX+NaOX+H_2O$$
$$3X_2+6NaOH=5NaX+NaXO_3+3H_2O$$

(X=Cl, Br and I)

Reaction with reducing agents. All these elements react with reducing agents. The oxidising power is in the order $F>Cl>Br>I$. Chlorine, bromine and iodine oxidises hydrogen sulphide to sulphur.

$$H_2S+X_2=2HX+S \quad X=Cl, Br \text{ and } I$$

Reaction with oxidising agents. Fluorine, chlorine and bromine do not react with most oxidising agents. Hydrogen peroxide, ozone and nitric acid oxidise iodine to iodic acid.

$$3I_2+10HNO_3=6HIO_3+10NO+2H_2O$$

Bleaching property. Fluorine destroys organic matters. Chlorine has strong bleaching property but bromine has weak bleaching action. Iodine has no bleaching property.

Formation of oxides and oxyacids. All these elements form oxides. Fluorine forms two oxides, viz., F_2O and F_2O_2. Chlorine forms four oxides, viz., Cl_2O, ClO_2, Cl_2O_6 and Cl_2O_7. Bromine forms the oxides, viz., Br_2O, BrO_2, $(Br_3O_8)_n$, etc. Iodine has two oxides, viz., I_2O_4 and I_2O_5.

Four oxy-acids of chlorine are known, viz., HOCl (hypochlorous acid), $HClO_2$ (chlorous acid), $HClO_3$ (chloric acid) and $HClO_4$ (perchloric acid). Two oxyacids of bromine are known, viz., HOBr (hypobromous acid), $HBrO_3$ (bromic acid). Iodine forms HIO (hypoiodous acid), HIO_3 (iodic acid) and HIO_4 (periodic acid). The halogen elements show different valencies in their oxides and oxy-acids.

Comparative study of hydracids of halogens. The hydrogen halides show resemblances in their physical and chemical properties. These properties change regularly from hydrofluoric acid to hydriodic acid.

(i) Except hydrogen fluoride all other hydrogen halides are colourless gaseous substance which fume in moist air. At ordinary temperature and pressure HF is a liquid.

All these compounds are covalent. Liquid hydrogen fluoride is associated through hydrogen bond formation. For this reason, its melting point and boiling point is higher than those of other hydrogen halides. The melting point and boiling point increase gradually from HCl to HI.

(ii) All these compounds are extremely soluble in water. Their solubilities in water increase gradually from HF to HI. They ionise in aqueous solution into hydrogen ion and halide ion.

$$HX \rightleftharpoons H^+ + X^- \quad (X = F, Cl, Br \text{ and } I)$$

(iii) Hydrogen fluoride is not thermally decomposed. Hydrogen chloride decomposes at 1500°C, hydrogen bromide at 800°C and hydrogen iodide at 180°C into their constituent elements.

(iv) Hydrogen fluoride does not react with oxidising agents. Oxidising agents oxidise hydrogen chloride into chlorine, hydrogen bromide into bromine and hydrogen iodide into iodine.

(v) HF and HCl do not react with conc. H_2SO_4, but HBr and HI are oxidised by conc. H_2SO_4 into bromine and iodine respectively.

$$H_2SO_4 + 2HBr = SO_2 + 2H_2O + Br_2$$
$$H_2SO_4 + 2HI = SO_2 + 2H_2O + I_2$$

Hence, the reducing power of these compounds increase gradually from HF to HI.

EXERCISES

1. How does fluorine occur and how is it isolated? Why is it impossible to liberate fluorine from aqueous solution of a fluoride?

2. How was fluorine isolated? Give reasons for the procedure adopted. Compare the properties of fluorine with those of chlorine. [C. U., '54]

3. Describe the preparation of fluorine from fluorspar describing carefully the apparatus used. Discuss the chemical properties of fluorine. State the uses of fluorine.

4. How is anhydrous hydrofluoric acid prepared? Distinguish between hydrogen fluoride and hydrofluoric acid. Discuss the action of hydrofluoric acid on glass. What do you mean by etching of glass?

5. "Hydrofluoric acid is a weak acid, yet it etches glass". Explain the statement.
Discuss the chemical properties of hydrofluoric acid.

6. What halogen does not form oxy-acids? Explain why it does not form oxy-acids similar to other halogens. Does this halogen form any compound with oxygen?

7. Describe the preparation of chlorine free from hydrogen chloride. What is the action of chlorine on (a) caustic soda (b) ammonium hydroxide (c) sulphurous acid (d) lime water and (e) water in which $CaCO_3$ is held in suspension?

8. How is a material bleached with chlorine? Discuss the uses of chlorine.

9. Give an account of the laboratory preparation of (a) hydrogen chloride and (b) solution of hydrogen chloride in water.

10. Give an account of the extraction of bromine from sea-water. How and under what conditions does bromine react with (a) hydrogen (b) sulphur dioxide and (c) phosphorus?

11. Discuss the reaction of halogens with water.

12. Describe the laboratory preparation of hydrobromic acid and hydriodic acid. Why cannot concentrated sulphuric acid be used in preparing HBr and HI from their salts ?

13. In the reactions : $Cl_2+2KI=2KCl+I_2$

$$I_2+2HClO_4=2HIO_4+Cl_2$$

explain why chlorine displaces iodine from KI and iodine displaces chlorine from $HClO_4$?

14. What are the chief sources of iodine ? Describe in details the extraction of iodine from these sources. Discuss the uses of iodine. Why does iodine sublime so quickly ?

15. Write the names of the following compounds $CaCl_2$; $Ca(ClO)_2$, $Ca(ClO_2)_2$, $Ca(ClO_3)_2$, $Ca(ClO_4)_2$. Calculate the oxidation number of chlorine in each compound.

16. You are given a source of chlorine and a solution of potassium hydroxide. How would you prepare crystals of potassium chlorate ?

17. You are given a mixture of KF, KCl, KBr and KI. What oxidising agent, would you use in order to liberate iodine from KI without the liberation of any other halogen ? After the liberation of iodine, what oxidising agents would you use to liberate only bromine and then only chlorine ? Can you oxidise the fluoride ? Explain your answer.

18. Discuss the differences between fluorine and chlorine. Explain what happens when chlorine gas is slowly passed through a solution containing potassium bromide and potassium iodide.

19. What happens when :

- (i) Iodine is heated with conc. nitric acid.
- (ii) Iodine is treated with mercury.
- (iii) Fluorine is passed into carbon tetrachloride.
- (iv) Chlorine is passed into hot caustic soda solution.
- (v) A mixture of sodium iodate and sodium iodide is acidified with hydrochloric acid.
- (vi) Calcium fluoride is heated with conc. H_2SO_4 in a glass vessel.
- (vii) Potassium bromide is heated with conc. H_2SO_4.
- (viii) A solution of potassium iodide is shaken with chlorine-water and carbon disulphide.
- (ix) Free iodine is treated with aqueous solution of KI.
- (x) Sodium silicate is treated with hydrofluoric acid.
- (xi) Fluorine is passed through sodium iodide solution.
- (xii) Iodine is treated with sodium thiosulphate solution.
- (xiii) Iodine is treated with chlorine-water.
- (xv) Bromine is added to moist red phosphorus.

20. Write the names of the following compounds :

(a) $HClO$ (b) $KClO$ (c) $KClO_3$ (d) $Ca(BrO)_2$ (e) $HClO_4$ (f) $Ca(IO_4)_2$ (g) $Ba(ClO_3)_2$ (h) $HClO_2$ (i) $NaBrO_3$ (j) $Mg(ClO_2)_2$. Calculate the oxidation number of halogens in each compound.

21. Explain the following statements :

- (a) Iodine replaces chlorine from chloric acid ($HClO_3$) and forms iodic acid (HIO_3).

(b) The reducing power of hydrogen iodide, hydrogen bromide and hydrogen chloride is in the order,

$HI > HBr > HCl$

(c) Hydrogen iodide cannot be prepared by the reaction of KI and conc. H_2SO_4 but hydrogen chloride can be prepared by the reaction of NaCl and conc. H_2SO_4.

(d) Chlorine liberates iodine from HI.

(e) In the preparation of HI from KI orthophosphoric acid can be used but conc. H_2SO_4 cannot be used.

(f) HF can associate but HCl cannot.

22. How would you prove that

(a) hydrogen chloride contains chlorine

(b) potassium chlorate contains chlorine and oxygen.

23. A mixture of MnO_2, conc. H_2SO_4 and a compound (B) is heated when a greenish yellow gas is evolved. The gas liberates iodine from potassium iodide solution and reacts with hot $NaOH^-$ solution to form the compound (B) and another compound (C). The compound (C) when heated liberates oxygen. Identify the compounds (B) and (C).

Ans. $B \rightarrow NaCl$, $C \rightarrow NaClO_3$

CHAPTER XI

INDUSTRIAL PREPARATION OF SOME CHEMICALS

(1) **Industrial preparation of hydrogen.** The major consideration in any industrial process is the cost of raw material. Because water is so abundant most of the industrial methods for the preparation of hydrogen are based on the decomposition of water. The principal methods for the manufacture of hydrogen are described below :

(a) **Steam-iron method (Lane's process).** The reaction between steam and red-hot iron is used for the manufacture of hydrogen. Steam is passed over spongy iron (obtained from the reduction of spathic iron ore) which is heated in vertical iron retorts to 650-800°C. Steam is decomposed by red-hot iron ; hydrogen is evolved and ferroso-ferric oxide is obtained.

$$3Fe+4H_2O \rightleftharpoons Fe_3O_4+4H_2$$

When the reaction stops and the evolution of hydrogen ceases the ferroso-ferric oxide Fe_3O_4 is reduced back to iron by passing water gas over it.

$$Fe_3O_4+4H_2 = 3Fe+4H_2O.$$

$$Fe_3O_4+4CO = 3Fe+4CO_2.$$

This iron can be used again for the decomposition of steam. Thus by the alternate use of steam and water gas, a small quantity of iron can be used almost indefinitely.

(b) **Bosch process or conversion method.** The method consists in passing steam over a layer of coke, coal or lignite which is heated to a white heat (1000° to 1100°C).

$$C+H_2O=CO+H_2$$

The product which is a mixture of equal volume of carbon monoxide and hydrogen is called water gas.

To separate hydrogen from carbon monoxide, water gas is mixed with steam and the mixture is passed over a suitable catalyst such as iron oxide with aluminium oxide as promotor at 400° to 500°C. The carbon monoxide reacts with steam forming hydrogen and carbon dioxide. This reaction, called the conversion of carbon monoxide, can be represented by the equation :

$$\underbrace{(H_2)+CO}_{\text{(water gas)}} + \underset{\text{(steam)}}{H_2O} \rightleftharpoons CO_2 + H_2 + (H_2)$$

The carbon dioxide formed is then separated from hydrogen by washing the gas mixture with water under a pressure of 20 atmospheres. Under this condition only carbon dioxide is soluble in water and hydrogen remains undissolved. Hydrogen obtained is nearly pure. The chief impurities are traces of carbon monoxide and carbon dioxide which can be removed by washing the gas with ammonical solution of cuprous formate. Large quantities of hydrogen are manufactured in this way.

Carbon monoxide can also be removed from the mixture by cooling it to around −200°C at which temperature carbon monoxide only liquefies while hydrogen remains in the gaseous state.

(c) **Hydrocarbon-steam method.** Natural gas consists mainly of methane (about 90 per cent) ; the rest being chiefly related hydrocarbons such as ethane C_2H_6, propane C_3H_8. It is mixed with steam and the mixture is passed over a mixture of finely divided nickel and cobalt which act as catalyst, at 870°C. The product is a mixture of carbon monoxide and hydrogen.

$$CH_4 + H_2O = CO + 3H_2$$

The mixture of carbon monoxide and hydrogen is passed over heated ferric oxide together with steam ; the ferric oxide acting as a catalyst. Carbon monoxide in the mixture is converted into carbon dioxide.

$$CO + H_2O = CO_2 + H_2$$

Carbon dioxide is then removed by being dissolved, under pressure, in water. This method of manufacturing hydrogen has been used more and more extensively in the past few years and is rapidly increasing in importance.

(d) **Electro chemical method.** If there is a source of cheap electric power at hand, this process of producing hydrogen is commercially feasible. The advantage of this process is the high purity of the product.

This process is carried out on a large scale using iron tanks containing 20% solution of sodium hydroxide in water. The electrodes consist of iron sheets. The anodes which are nickel plated to resist anodic oxidation and the cathodes are arranged in pairs. The electrodes are separated from each other by porous asbestos partition which prevent the mixing of the gases. The end plates are connected to the source of electricity when electric current passes through the solution. The hydrogen and oxygen liberated at alternate sides of the plates pass through suitable passage into collecting pipes.

(2) **Industrial preparation of ammonia.** Ammonia is prepared on the industrial scale as a by-product of coal distillation, by the

hydrolysis of calcium cyanamide and by the direct combination of nitrogen and hydrogen (Haber's process).

(a) **Ammonia from coal.** Ammonia can be obtained commercially as a by-product of the carbonisation of coal. Coal contains about 1 to 2 per cent nitrogen. When coal is subjected to destructive distillation, a large portion of the nitrogen escapes as ammonia. This is then separated from other gaseous products of distillation by passing the mixture through water in which ammonia is absorbed partly as free ammonia and partly as salts such as the carbonate, sulphide, cyanide, etc. Ammonia is liberated from this ammoniacal liquor by heating with lime. Ammonia thus produced is passed into sulphuric acid, when a solution of ammonium sulphate results, from which the crystals of the salt can be obtained. Ammonium sulphate is used as a fertiliser. Pure ammonia can be obtained by heating ammonium sulphate with lime.

(b) **Cyanamide process.** Considerable quantities of ammonia are prepared from calcium cyanamide. Calcium cyanamide is obtained by passing nitrogen gas over crushed calcium carbide containing a little calcium chloride heated at 1100°C by carbon rods in an electric furnace. Calcium cyanamide mixed with graphite is formed as a dark grey mass called nitrolim or "cyanamide".

$$CaC_2 + N_2 = CaCN_2 + C$$

Calcium cyanamide thus formed is pulverised and treated first with cold water to convert any unreacted calcium carbide to acetylene. Finally, it is treated with steam under a pressure of 3 atmospheres in presence of little added base in autoclaves (i.e., pressure digesters). The base facilitates the liberation of ammonia.

$$CaCN_2 + 3H_2O = CaCO_3 + 2NH_3$$

Ammonia evolved is then driven out by increasing the pressure of steam gradually to 11 atmospheres and the temperature to 180°C. Calcium cyanamide may be used directly as a fertiliser.

(c) **Haber's synthetic process.** At ordinary temperatures, nitrogen does not combine with hydrogen but if electric sparks are passed through a mixture of these gases, a small quantity of ammonia forms. A detailed investigation of this reaction has revealed that the sparks cause not only the formation of ammonia, but its decomposition back into nitrogen and hydrogen as well. Thus, the reaction between hydrogen and nitrogen is reversible and is represented by the equation.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

This is an exothermic reaction (i.e., heat is evolved during the reaction) and is accompanied by the reduction in volume.

$$\underset{(1\text{ vol.})}{N_2} + \underset{(3\text{ vols.})}{3H_2} \rightleftharpoons \underset{(2\text{ vols.})}{2NH_3} + \underset{\text{reduction}=2\text{ vols.}}{22000\text{ calories}}$$

Since the formation of ammonia leads to a decrease in the volume of the nitrogen-hydrogen mixture, an increase in pressure should favour the formation of ammonia. Again, since the reaction is exothermic, the lower is the temperature, the higher is the yield of ammonia. Hence, in order to get appreciable amounts of ammonia, the reaction must be carried out at as low a temperature as possible. But, at low temperatures the gases react very slowly. Hence, the reaction is carried out at a temperature called the optimum temperature at which neither the speed of the reaction is too slow nor the yield of ammonia is too low. The optimum temperature for this reaction is found to be 500°C. At this temperature, the speed of the reaction is satisfactorily increased by the use of catalysts. The most satisfactory catalyst now in use is spongy iron which contains small amounts of a highly basic oxide such as potassium oxide, K_2O and of an amphoteric oxide such as aluminium oxide, Al_2O_3. These oxides serve as promoters. Traces of carbon monoxide, hydrogen sulphide, etc., poison the catalysts and these substances must be carefully removed from the reaction mixture.

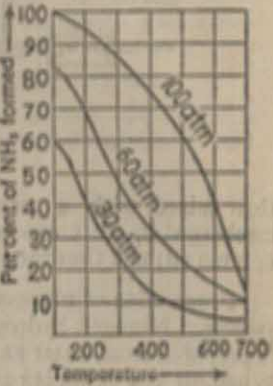

Fig. 11.1

In practice, the reaction is carried out in the presence of the catalyst at 400°C to 500°C and under 100 to 1000 atmospheres. Fig. 11.1 illustrates how the yield of ammonia changes with temperature and pressure.

A mixture of pure and dry hydrogen and nitrogen in the ratio of 3 : 1 by volume is compressed by means of compressor (A) to 200 to 300 atm. The gases then pass over the catalysts in the synthesis column (B) heated by an electric current to 500 or 550°C. Hydrogen combines with nitrogen in the synthesis column to form ammonia. The heat given off during the reaction serves to maintain the necessary temperature once the process has got under way. The gases leaving the synthesis column, contain about 20 per cent ammonia and enter into the cooler (C) where the gases are cooled and gaseous ammonia liquefies due to high pressure and cooling; nitrogen and hydrogen are not liquefied. The liquid ammonia is then collected into the separator (D) from which it is transferred by batches into low-pressure collector (E). From the collector it goes to the storage. The unchanged nitrogen and hydrogen are drawn out of the separator (D) by the circulation pump (F). They are

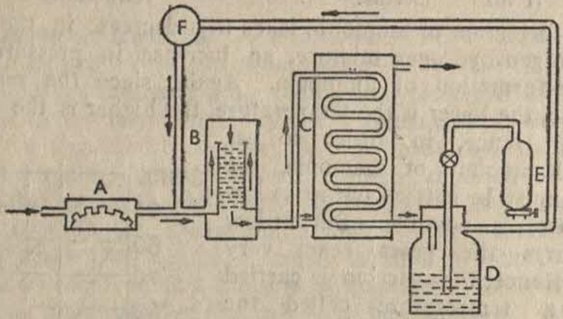

Fig. 11.2

then mixed with a new portion of nitrogen-hydrogen mixture discharged by the compressor (A) and pass back into the synthesis column (B) and thus the process continues.

Preparation of nitrogen-hydrogen mixture in the ratio of 1 : 3 by volume. Nitrogen-hydrogen mixture used in the Haber's process is prepared from water gas ($CO+H_2$) and producer gas ($CO+N_2$). When air and steam is passed over heated carbon producer gas and water gas are respectively formed.

$$2C+(N_2+O_2)=2CO+N_2$$

$$C+H_2O=CO+H_2$$

Producer gas, water gas and steam are next mixed in such a proportion that nitrogen and hydrogen in the final mixture remain in the ratio of 1 : 3 by volume after the removal of carbon monoxide. The mixture is passed over the mixture of ferric oxide and chromic oxide (catalyst) heated to 450°C when carbon monoxide is oxidised to carbon dioxide.

$$CO+H_2O=CO_2+H_2$$

The resulting gas mixture is next passed into water under a pressure of about 25 atmospheres. Under this condition, only carbon dioxide is dissolved in water and nitrogen-hydrogen mixture remain undissolved. Nitrogen-hydrogen mixture thus obtained contain traces of carbon monoxide and carbon dioxide which are removed by washing the mixture with ammoniacal solution of cuprous formate. The mixture is dried before use in the Haber's process.

At present most industrial ammonia is prepared by Haber's process. The principal advantage of this method is that it is comparatively cheap.

(3) **Industrial preparation of nitric acid.** Three methods are available for the manufacture of nitric acid, viz.,

(a) by distillation of sodium nitrate (Chile saltpetre) and concentrated sulphuric acid.

(b) catalytic oxidation of ammonia—Ostwald process.

(c) from air—Birkeland and Eyde process.

(a) **By distillation of sodium nitrate and concentrated sulphuric acid.** Sodium nitrate (Chile saltpetre) is obtained in enormous quantities from the nitre beds of Chile and Peru. On a large scale nitric acid is manufactured by distilling Chile saltpetre and conc. sulphuric acid.

$$2H_2SO_4 + 3NaNO_3 = NaHSO_4 + Na_2SO_4 + 3HNO_3$$

This method is still used to some extent. One or two tons of Chile saltpetre and more than this weight of concentrated sulphuric acid are taken into a large cast-iron retort (Fig. 11.3). The retort is then heated in the furnace. The vapours of nitric acid which are evolved pass through the outlet of the retort into silica pipes cooled by water and condense yielding conc. HNO_3. The gases and vapours of nitric acid which are not condensed into pipes pass into a tower packed with stoneware balls down which a stream of water trickles. The vapour, and the nitrogen dioxide produced by the decomposition of nitric acid are absorbed by water yielding dilute nitric acid. $4NO_2 + O_2 + 2H_2O = 4HNO_3$

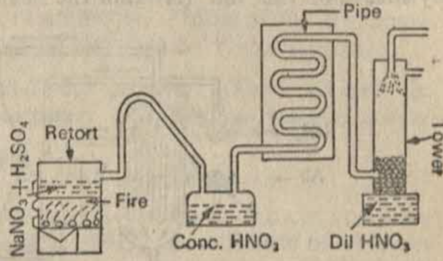

Fig. 11.3

The residue left in the retort is run out in the fluid state from an outlet at the bottom. It is a mixture of sodium hydrogen sulphate and sodium sulphate. When solid, the mixture is known as nitre cake.

Nitre cake is used in the manufacture of sodium sulphate and hydrochloric acid.

(b) **Catalytic oxidation of ammonia. Ostwald process.** The Ostwald process has largely replaced the older one. At present, it is the chief industrial method for preparing nitric acid.

In this method, a mixture of ammonia and excess of air is passed rapidly over platinum gauze catalyst heated to 800°C when nitric oxide is formed.

$$4NH_3 + 5O_2 = 6H_2O + 4NO + 216 \text{ kcal}$$

The reaction is highly exothermic and hence once the reaction is started, the heat evolved in the reaction is sufficient to maintain the temperature. The nitric oxide formed reacts, after cooling, with the excess oxygen present in air to form nitrogen dioxide.

$$2NO+O_2=2NO_2$$

Nitrogen dioxide is then dissolved in water to form nitric acid.

$$3NO_2+H_2O=2HNO_3+NO$$

Nitric oxide liberated is re-oxidised to nitrogen dioxide by air. More than 90% of ammonia is converted into nitric oxide. At present, an alloy of platinum and rhodium containing 5—10% rhodium is more often used and the yield of nitric oxide is then 96 to 98 per cent.

Fig. 11.4 is a diagram of ammonia oxidation plant. Air freed from dust particles by filtration through woollen cloth is blown by means of the fan (A) into the heat exchanger (B) where it is heated by the hot gases discharged from the catalyst furnace (E). From the heat exchanger it enters into the mixer (C). Dry and pure ammonia is blown by the fan (D) into the same mixer.

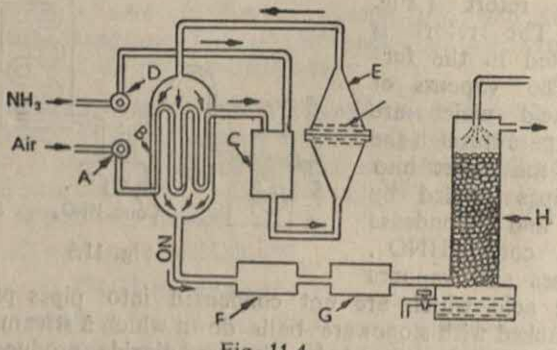

Fig. 11.4

From the mixer (C), ammonia-air mixture containing 10-11 per cent ammonia enters into the catalyst furnace (E) which contains several layers of fine-mesh gauze made of an alloy of platinum and rhodium. The rate of flow and the temperature of the catalyst are carefully controlled ; otherwise ammonia is oxidised to nitrogen and efficiency of the process is lowered.

$$4NH_3+3O_2=2N_2+6H_2O$$

The gases are heated electrically by the resistance wire just above the catalyst in order to start the reaction. Once the reaction has started, the heater is turned off since the heat evolved in the reaction maintains the necessary temperature. In the catalyst furnace (E), ammonia is oxidised into nitric oxide. The mixture of the hot gases passes from the catalyst furnace to the heat exchanger (B) where it heats the incoming air and is itself cooled to 500—550°C. The gases leaving the heat exchanger pass consecutively into cooler (F) and tower (G) where oxidation of nitric oxide to nitrogen dioxide takes place. The mixture of nitrogen dioxide and other gases then pass into absorption towers made up of stainless steel, packed with broken quartz down which a stream of water trickles. Nitrogen dioxide is absorbed in water to form nitric acid. Acid collected at the bottom of the tower contains about 50 to 55 per cent HNO_3.

The acid may be concentrated to 98% by distillation with conc. sulphuric acid. 98% nitric acid can also be prepared by the reaction between water or the dilute acid, liquid N_2O_4 and oxygen under a pressure of 50 atms. This method called the "direct synthesis" is carried out at 70°C.

At present most of the vast quantities of nitric acid are manufactured by the oxidation of ammonia. Most of the ammonia for the purpose is prepared from its elements by Haber's process.

(c) **From air. Birkeland-Eyde process.** This method is based on the direct union of nitrogen and oxygen forming nitric oxide.

$$N_2 + O_2 \rightleftharpoons 2NO - 43{\cdot}2 \text{ kcal}$$

Since this reaction is highly endothermic, it is more complete at very high temperatures. Consequently, the mixture of nitrogen and oxygen is heated to very high temperatures (about 3000°C) to cause the combination and the product is cooled very rapidly below 1200°C to keep the nitric oxide formed from decomposing back into nitrogen and oxygen.

The usual means of obtaining such high temperatures is by the use of electric arc which produces a temperature of about 4000°C. If the flame of the electric arc is brought between the two poles of a strong electromagnet, it becomes disc-shaped (fig. 11.5) and the surface of it is greatly increased. When a stream of air is passed rapidly through the arc, it becomes very hot at the moment it comes in contact with the flame, after which its temperature drops instantly below 1200°C. When the product is cooled further, nitric oxide combines with oxygen to form nitrogen dioxide. Nitrogen dioxide is dissolved in water to form nitric acid.

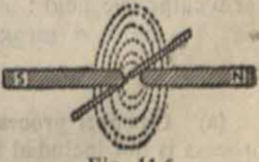

Fig. 11.5

$$2NO + O_2 = 2NO_2$$
$$3NO_2 + H_2O = 2HNO_3 + NO$$

Fig. 11.6 is a diagram of the arc process. Air freed from mechanical impurities by filtration is blown by means of the blower (1) through a flat circular furnace (2). Inside the furnace an alternating current electric arc burning between water-cooled copper poles is spread by means of an intense magnetic field into a disc of "flame." In the flame, part of air combines into nitric oxide. The gases which leave the furnace at about 1000°C containing about 1% nitric oxide now pass into the cooler (3) and boiler (4). In the boiler the gases are cooled to 150°C with the production of steam. The gases are finally cooled to 50°C by passage through large aluminium pipes exposed to air. The gases then enter into the oxidising tower (5) where NO is oxidised to NO_2. NO_2 is absorbed by water in the absorption tower (6) forming nitric acid.

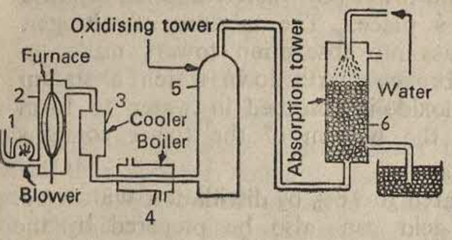

Fig. 11.6

The manufacture of nitric acid by this process requires a great amount of electric power. In 1902, the method was extensively carried out in Norway which possesses vast resources of cheap electric power. At present the method is obsolete.

(4) **Industrial preparation of sulphuric acid.** Sulphuric acid is manufactured by two methods, viz., (a) Chamber process and (b) Contact process. In both the processes, sulphur dioxide is oxidised by atmospheric oxygen in presence of a suitable catalyst to sulphur trioxide. Sulphur trioxide is then dissolved in water to form sulphuric acid :

$$2SO_2 + O_2 = 2SO_3$$
$$SO_3 + H_2O = H_2SO_4$$

(a) **Chamber process.** This process is now obsolete. As the process is not included in the syllabus, it is not discussed here.

(b) **The contact process.** In this process, sulphur dioxide is catalytically oxidised to sulphur trioxide by atmospheric oxygen ; sulphur trioxide is then dissolved in water to form sulphuric acid. However, if SO_3 is passed directly into pure water, so much heat is produced that it leads to the formation of fog consisting of droplets of H_2SO_4 solution. This technical difficulty is avoided by absorbing sulphur trioxide into 96 to 98% sulphuric acid in which it dissolves smoothly. The solution of SO_3 in sulphuric acid is then diluted by adding water at such a rate that the final solution is maintained at a concentration of 97 to 99%. These reactions can be represented by the following series of equations :

$2SO_2+O_2 \rightleftharpoons 2SO_3$ (catalytic oxidation of SO_2)

$SO_3+H_2SO_4=H_2S_2O_7$ (solution of SO_3 in sulphuric acid)

$H_2S_2O_7+H_2O=2H_2SO_4$ (dilution with water)

The fundamental reaction of contact process is the combination of sulphur dioxide with oxygen :

$$2SO_2+O_2 \rightleftharpoons 2SO_3+45 \text{ kcal}$$

This is an exothermic reversible reaction. Hence, at low temperatures the reaction proceeds nearly to completion and a satisfactory yield of sulphur trioxide can be obtained. But at low temperatures, the rate of the reaction is very slow and at high temperatures where the rate is satisfactory, the yield is low because of the reverse reaction leading to the decomposition of sulphur trioxide. For this reason, an optimum temperature of 450°C is maintained in the contact apparatus ; below this temperature the gases combine too slowly and above this temperature the back reaction is accelerated.

At the optimum temperature, certain catalysts such as platinum and vanadium pentoxide speed up the reaction without altering the equilibrium. The catalyst formerly used was finely divided platinum but it was very expensive and easily poisoned by impurities such as arsenious oxide, sulphuric acid fog and dust present in the gases from pyrite burners. The catalyst now used is vanadium pentoxide V_2O_5, which is almost as active as platinum but is cheaper and is not so easily poisoned. These catalysts are of the heterogeneous or contact type, hence the name of the process.

The increase of oxygen concentration in the mixture increases the yield of sulphur trioxide by shifting the equilibrium of the reaction to the right. If K is the equilibrium constant of the reaction, then

$$K=\frac{[SO_3]^2}{[SO_2]^2[O_2]}$$

If the concentration of oxygen is increased, the concentration of sulphur trioxide will increase as K is constant at a constant temperature. In other words, the yield of SO_3 will increase. In practice, by passing sulphur dioxide with an excess of oxygen over the catalyst at 450°C, about 97 per cent of sulphur dioxide is converted into sulphur trioxide.

The sulphur dioxide for this process is obtained either by burning sulphur or by roasting metal sulphides, chiefly pyrites,

FeS_2, in a current of air in special burners. The gases from the burners (1) containing a mitxture of sulphur dioxide and air are passed through cooler (2) where they are cooled and washed with a fine spray of water. The gases leaving the cooler are next passed through an electrostatic separator (3) to remove dust, fog and suspended particles. They are then passed to wash tower (4) where they are showered with lime water to remove last traces of chlorine. The gases from the wash tower are passed up the scrubbers or drying towers (5) packed with coke down which concentrated sulphuric acid is flowing. Here they are washed with sulphuric acid and dried. Finally, the gases are freed from acid mist by passing through the coke box (6). The purified and dried gas must be free from fog and perfectly clear and no suspended particles and fog must be seen when a powerful beam of light is passed through it in the chamber (6) ("optically clear" gas). The purified gases then pass through a special preheater (7) where it is heated by the gases (sulphur trioxide and nitrogen) discharged from the contact apparatus and then enters the contact apparatus (8) containing the catalyst. The contact apparatus is a large cylinder with four grate-like shelves which are covered with the catalysts. The gases enter the apparatus at the top and pass through layers of the catalysts when sulphur dioxide is oxidised to sulphur trioxide. The temperature in the apparatus is kept at about 450°C. Since the reaction is exothermic, it continues without the application of external heat after once it has been started.

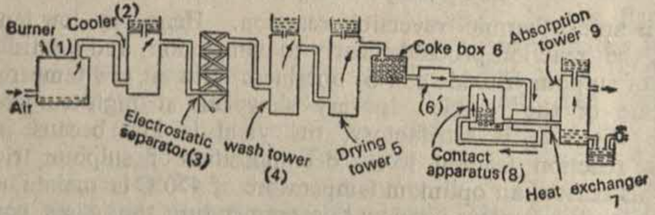

Fig. 11.7

The gases leaving the contact apparatus consist principally of sulphur trioxide and nitrogen. They are then passed into the absorption tower (9) where sulphur trioxide is absorbed into 96 to 98 per cent sulphuric acid. Water cannot be used in the absorber because an acid mist is formed by the direct contact with the sulphur trioxide which is almost impossible to absorb. The solution in the absorption tower is maintained at a concentration of 96 to 98% by a regulated influx of water.

If water is not added, then sulphur trioxide dissolves in sulphuric acid forming highly concentrated acid known commercially as *fuming sulphuric acid* or *oleum* which may contain as much as 70% of dissolved sulphur trioxide. Very pure sulphuric acid of any desired concentration can be prepared by diluting oleum with water.

Fuming sulphuric acid or Oleum. When sulphur trioxide is passed into 98% sulphuric acid, a highly concentrated sulphuric acid known as fuming sulphuric acid or oleum is formed. Sulphuric acid of different concentrations are prepared by diluting oleum with water.

Fuels

Fuels are those materials which undergo combustion with oxygen of the air to liberate heat which can be employed for heating, for preparing food and for many industrial processes. Coal, coke, wood, charcoal, etc., are solid fuels ; petroleum, kerosene, etc., are liquid fuels and producer gas, water gas, coal gas, etc., are gaseous fuels.

Destructive distillation. When some solid substances are heated to a high temperature in absence of air, they undergo chemical decomposition into volatile and non-votatile compounds. Volatile compounds are then separated from non-volatile compounds by the method of distillation. The non-volatile compounds are left in the distilling chamber. Destructive distillation is a process in which a substance is chemically decomposed into volatile and non-volatile compounds by heating it in a closed vessel in absence of air and volatile products are then separated from the non-volatile products by distillation. Destructive distillation of coal is known as carbonization of coal. In destructive distillation, the substance undergoes chemical change and the volatile substance given off distils, but in ordinary distillation, the substance does not undergo any change.

(5) **Coke-oven or Coal gas.** Coal gas is a mixture of various combustible gases produced by the destructive distillation of coal (i.e., distillation out of contact with air). Its composition depends on the raw meterials but on the average it may be expressed by the following figures.

Hydrogen	...	55%
Methane	...	30%
Carbon monoxide	...	4%
Other hydrocarbons (ethylene, acetylene and benzene.)	...	3%
Incombustible impurities (CO_2, N_2, O_2)	...	8%

Besides coal gas, other products which are obtained during the destructive distillation of coal are : tar (containing benzene, toluene, naphthalene, phenol and related organic compounds) ; ammoniacal liquor, coke and gas carbon.

Manufacture of coal gas. Bituminous coal is heated in fire-clay horizontal retorts out of contact with air ; the heating is done by the combustion of producer gas generated in producers built immediately beneath the retorts. During heating, the complex organic compounds in the coal are decomposed into coke, coal gas and volatile products. The coal gas and volatile products pass from the retorts by way of vertical ascension pipes into horizontal hydraulic main where tar and water are condensed. The excess of tar flows into a tar-pit. The hot gases and vapours next pass through a series of pipes called condensers where the gases are cooled to atmospheric temperature and more tar is condensed. The liquids collected in the tar-pit separate into two layers—the lower is coal tar and upper is gas liquor which contains an aqueous solution of ammonia and ammonium compounds. The cooled gas then passes from the condensers to the scrubber which is an iron tower filled with coke down which a spray of water trickles. The spray of water removes from the gas all traces of NH_3, and some HCN, H_2S and CO_2. The gas passes from the scrubbers to the purifiers which are iron boxes fitted with horizontal shelves and (i) containing slaked lime in which mainly CO_2 and also H_2S, CS_2, HCN, etc., are absorbed and (ii) hydrated ferric oxide which removes completely H_2S and HCN from the gas.

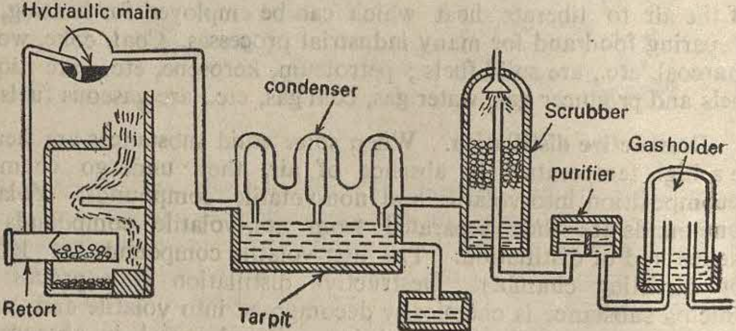

Fig. 11.8

$$2Fe(OH)_3 + 3H_2S = Fe_2S_3 + 6H_2O$$

$$Fe_2O_3 + 6HCN = 2Fe(CN)_3 + 3H_2O$$

The oxide of iron is revived from time to time by exposure to air.

$$2Fe_2S_3 + 3O_2 = 2Fe_2O_3 + 6S$$

The oxide can be used until it contains about 50% of sulphur. From the purifiers, the gas passes to the gas holders where it is stored over water and piped to the consumer.

It is very difficult to remove carbon disulphide from the coal gas completely. It is sometimes converted into hydrogen sulphide, and carbon by passing the gas over finely divided nickel at 400°C.

$$CS_2 + 2H_2 = 2H_2S + C$$

The hydrogen sulphide is then removed as above.

Coal gas is a colourless gas having peculiar smell. If the poisonous impurities such as HCN, H_2S, etc., are not removed completely from coal gas, then it will be poisonous. It burns in air with a smoky flame producing carbon dioxide and water. It is very slightly soluble in water. Coal gas is used for illuminating purposes and as a fuel.

By-products of coal gas manufacture. During the manufacture of coal gas, numerous valuable by-products are produced. Among these are coal tar, ammoniacal liquor, coke, gas carbon and spent oxide of iron.

(i) **Coal tar.** The tar is a complex mixture containing many valuable organic compounds. It owes its black colour to suspended particles of carbon. When tar is subjected to fractional distillation, benzene, toluene, naphthalene, phenol, creosote oil, anthracene oil or green oil, etc., are obtained. These compounds are the starting material for the manufacture of numerous dyes, drugs, perfumes and explosives. The residue left after distillation is pitch. Pitch is used for road making.

(ii) **Ammoniacal liquor.** The ammoniacal liquor is boiled with excess of lime and ammonia evolved is passed into sulphuric acid to form ammonium sulphate. Ammonium sulphate is used as a fertiliser.

(iii) **Coke.** It is left in the retort after the destructive distillation of coal. It is used as a valuable fuel and in metallurgical and other industrial operations.

(iv) **Gas carbon.** It is obtained as a hard dense deposit of almost pure carbon which collects on the inside of the retort. It is a good conductor of electricity and is used in making electrodes.

(v) **Spent oxide of iron.** It is used for the manufacture of ferrocyanide and for the recovery of sulphur.

EXERCISES

1. Discuss the contact process for the manufacture of sulphuric acid mentioning the physico-chemical principles involved in the process. [H. S., '80]

2. Discuss the manufacture of ammonia by Haber's process, mentioning the physico-chemical principles involved in the process.

3. Discuss the manufacture of nitric acid by Ostwald's process. [H. S., '79]

4. What are fuels? What is destructive distillation? Describe the manufacture of coal-gas.

APPENDIX

Example 1. A mixture of three gases A, B and C are passed first into an acidified dichromate solution when A is absorbed turning the solution green. The remainder of the gas is passed through an excess of lime water which turns milky, resulting in the absorption of B. The residual gas C is absorbed by an alkaline pyrogallol solution. However, the original gaseous mixture does not turn the lead acetate paper black. Identify A, B and C. [I.I.T.,'74]

Solution : Both sulphur dioxide and hydrogen sulphide reduce acidified dichromate solution. But since the original mixture does not turn lead acetate paper black, the gas A must be sulphur dioxide.

$$K_2Cr_2O_7+3SO_2+H_2SO_4=K_2SO_4+Cr_2(SO_4)_3+H_2O$$

The gas B must be carbon dioxide since it turns lime water milky and does not react with acidified dichromate solution.

$$Ca(OH)_2+CO_2=CaCO_3+H_2O$$

Since the gas C is absorbed by alkaline pyrogallol solution it must be oxygen. Hence,

A is sulphur dioxide (SO_2)
B is carbon dioxide (CO_2)
C is oxygen (O_2)

Example 2. A colourless solid compound (A) on heating gives a solid compound (B) and oxygen. (B) on treatment with dilute hydrochloric acid evolves a brown gas. Again (B) on heating with ammonium chloride gives a colourless gas and a residue (C). Also on heating (A) with ammonium chloride a colourless gas is evolved and a residue is obtained which is same as (C). This residue gives a yellow colour in the bunsen flame. Identify the compounds (A), (B), (C) and write equations for all the reactions. [J.E.E., '86]

Solution : Since the residue (C) gives a yellow colour in the bunsen flame, it is a sodium salt. Now, (C) is formed as a result of the reaction of (A) with ammonium chloride and also as a result of the reaction of (B) with ammonium chloride. Therefore, (A) and (B) must be sodium salt. Again, (A) decomposes, on being heated to give (B) and oxygen. (B) reacts with dil. HCl to give brown fumes. Hence, (B) must be sodium nitrite and (A) is sodium nitrate. The reactions are :

$$\underset{(A)}{2NaNO_3}=\underset{(B)}{2NaNO_2}+O_2$$

$$2NaNO_2+2HCl=2NaCl+H_2O+NO+\underset{\text{(brown)}}{NO_2}$$

That (B) is sodium nitrite is confirmed by the fact that it gives a colourless gas (nitrogen) on being heated with ammonium chloride. Similarly, the formation of a colourless gas (nitrous oxide) confirms that (A) is sodium nitrate. The reactions are :

$$\underset{(B)}{NaNO_2}+NH_4Cl=\underset{(C)}{NaCl}+N_2+2H_2O$$

$$NaNO_3+NH_4Cl=NaCl+N_2O+2H_2O$$

Hence, A is sodium nitrate ($NaNO_3$)

B is sodium nitrite ($NaNO_2$)

C is sodium chloride (NaCl)

Example 3. A compound A on heating with excess of caustic soda solution liberates a gas B which gives white fumes on exposure to HCl. Heating is continued to expel the gas completely. The resultant alkaline solution again liberates the same gas B when heated with zinc powder. However, the compound A, when heated alone, does not give nitrogen. Identify A and B. [I.I.T., '73]

Solution. (i) Since the compound A on being heated with excess of NaOH, gives the gas B which forms white fumes with HCl, the gas B must be NH_3 and the compound A must be an ammonium salt.

(ii) The resultant alkaline solution when heated with zinc powder gives NH_3. Hence, the solution contain either sodium nitrite ($NaNO_2$) or sodium nitrate ($NaNO_3$).

(iii) The compound A does not give nitrogen on heating. Therefore, the compound A must be ammonium nitrate (NH_4NO_3).

Thus : A is ammonium nitrate (NH_4NO_3)

B is ammonia (NH_3)

Example 4. A soft white metal (A) (atomic number 11) is dropped into water when a compound (B) (soluble in water) and a gas (C) are formed. When the gas (C) is passed over heated copper oxide, metallic copper and water are formed. When the aqueous solution of the compound (B) is added to zinc sulphate solution compound (D) is precipitated. The compound (D) dissolves in excess of the aqueous solution of (B). Identify the compounds A, B, C and D giving the chemical reactions involved in each step.

Solution : The metal (A) is soft and its atomic number is 11. It reacts with water to form the gas (C) and the compound (B). The gas (C) reduces copper oxide to metallic copper and water is formed. Hence, the gas (C) must be hydrogen since water contains only two elements, viz , oxygen and hydrogen. Hence, the metal (A) must be sodium and the compound (B) is sodium hydroxide.

$$\underset{(A)}{2Na}+2H_2O=\underset{(B)}{2NaOH}+\underset{(C)}{H_2}$$

The compound B (sodium hydroxide) reacts with zinc sulphate to form a precipitate (D). The precipitate (D) dissolves in excess of sodium hydroxide. Hence, the precipitate (D) must be zinc hydroxide.

$$ZnSO_4 + 2NaOH = \underset{\substack{\text{ppt}\\(D)}}{Zn(OH)_2} + Na_2SO_4$$

$$Zn(OH)_2 + 2NaOH = \underset{\substack{\text{sodium}\\\text{zincate}}}{Na_2ZnO_2} + 2H_2O$$

Hence, A is sodium (Na)
B is sodium hydroxide (NaOH)
C is hydrogen (H_2)
D is zinc hydroxide, $Zn(OH)_2$

Example 5. When a mixture of a potassium salt (A) and a black solid (B) is heated, a white solid (C) is formed and a gas (D) is evolved. After the reaction (B) remains unchanged both in mass and in chemical composition. When (A) is alone heated, it decomposes into (C) and(D)but very slowly. When aqueous solution of silver nitrate is added to the aqueous solution of the salt (C), a white precipitate of (E) is obtained. (E) is completely soluble in ammonium hydroxide. The gas (D) forms a brown coloured gas (F) with nitric oxide and is soluble in alkaline pyrogallate solution. Identity A, B, C, D, E and F giving reactions involved in each step. What is the function of B ?

Solution. The gas (D) forms a brown coloured gas with nitric oxide and is soluble in alkaline pyrogallate solution. So it is oxygen and the brown coloured gas is nitrogen dioxide.

$$2NO + \underset{(D)}{O_2} = \underset{(F)}{2NO_2}$$

The gas (D) is formed when the mixture of (A) and (B) is heated. (B) remains unchanged both in mass and in chemical composition. So it acts as a catalyst. Since (B) is black, it is manganese dioxide.

Again, the white solid (C) which is formed by the decomposition of (A) gives with silver nitrate a white precipitate (E) which is soluble in ammonium hydroxide. Hence, the white solid (C) must be potassium chloride. (A) when heated alone slowly decomposes into (C) and (D). Hence (A) must be potassium chlorate. The white precipitate is silver chloride.

$$\underset{(A)}{2KClO_3} + \underset{(B)}{[MnO_2]} = \underset{(C)}{2KCl} + \underset{(D)}{3O_2} + [MnO_2]$$

$$KCl + AgNO_3 = \underset{\substack{\text{ppt}\\(E)}}{AgCl} + KNO_3$$

Hence, A is potassium chlorate ($KClO_3$)
B is manganese dioxide (MnO_2)
C is potassium chloride (KCl)
D is oxygen (O_2)
E is silver chloride ($AgCl$)
F is nitrogen dioxide (NO_2)

Example 6. The hardness of a sample of water is 10°. What is the amount of $CaCO_3$ present in that sample of water ? Express 1° hardness in terms of $CaCO_3$ per 10^5 parts of water by weight and in terms of milligram equivalent of Ca^{++} ions or Mg^{++} ions per litre.

Solution. 1 ppm $\equiv$ 1 mg of $CaCO_3$ in 1 litre of water.

$\therefore$ 100 ppm $\equiv$ 100 mg of $CaCO_3$ in 1 litre of water.

$\therefore$ 10° $\equiv$ 100 mg of $CaCO_3$ in 1 litre of water.

Now, 1° $\equiv$ 10 mg of $CaCO_3$ in 1 litre of water.

Again, 100 mg of $CaCO_3$ contain 40 mg of Ca^{++} ions.

Now, 40 mg of Ca^{++} ions $\equiv$ 2 mg-equiv of Ca^{++} ions or Mg^{++} ions.

$\therefore$ 10 mg of $CaCO_3 \equiv \frac{2\times10}{100} \equiv 0{\cdot}2$ mg-equiv of Ca^{++} ions or Mg^{++} ions.

$\therefore$ 1° hardness $\equiv$ 0·2 mg-equiv of Ca^{++} ions or Mg^{++} ions per litre.

1° hardness $\equiv$ 1 gram of $CaCO_3$ in 10^5 grams of water.

Example 7. Calculate in grams per litre the amount of hydrogen peroxide which is of "10 volume" strength. What is the normality of the solution ?

Solution : 1 volume of hydrogen peroxide is of $\frac{1}{3{\cdot}294}$ per cent strength.

$\therefore$ 10 volume of hydrogen peroxide is of $\frac{10}{3{\cdot}294}$ per cent strength.

$\therefore$ 100 c.c of the solution contain $\frac{10}{3{\cdot}294}$ grams of hydrogen peroxide.

$\therefore$ 1000 c.c of the solution contain $\frac{10\times10}{3{\cdot}294} = 30{\cdot}4$ grams of hydrogen peroxide.

$\therefore$ Amount of hydrogen peroxide per litre $=$ 30·4 grams.

Now, the equivalent weight of hydrogen peroxide is 17. Hence, the normality of the solution $=\frac{30{\cdot}4}{17}=1{\cdot}79$.

Example 8. Prove that under the same conditions of temperature and pressure equal volumes of all gases contain the same number of moles or molecules.

Solution : From the equation of state, we have $PV=nRT$ where P is the pressure of the gas, V is the volume of the gas and T is the temperature in the absolute scale and n is the number of moles.

$$\therefore\ n=\frac{PV}{RT}$$

Now, if P, V and T are the same for the gases, then n will be the same since R is a constant. In other words, equal volumes of all gases under the same conditions of temperature and pressure will contain the same number of moles or molecules.

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HIGHER SECONDARY EXAMINATION

1984

CHEMISTRY—First Paper

Group—A

1. (a) How will you completely separate the individual constituents of a mixture consisting of common salt, ammoniun chloride and sand ?

(b) Calculate the weight of one magnesium atom. (Mg = 24)

Or, (a) 24 gms. of a solid element require 44·8 litres of oxygen at N.T.P. for its complete conversion into a gaseous oxide. The gaseous oxide occupies a volume of 44·8 litres at N.T.P. What is the weight in gms. of the gaseous oxide produced and what is its vapour density ?

(b) Calculate the number of molecules of water present in 1·8 c.c. of water at 4°C.
3 + 2 = 5

2. (a) State Gay-Lussac's Law of gaseous volume.

(b) Show the nature of graph that would be obtained when the volume of a given mass of a gas at constant pressure is plotted against the temperature on the centigrade scale. Indicate the point on this graph which corresponds to the zero of the absolute scale of temperature.

(c) $PV = RT$. State why this equation is called the molar gas equation. Write the individual values at the standard condition of P,V and T of the gas equation $PV = RT$ in the C.G.S. units and hence calculate the value of the Molar Gas Constant in the C.G.S. unit. (d) 112·0 gms. of pure iron are completely converted into ferric chloride dissolved in water. How many litres of H_2S gas at N.T.P. will be required to convert this entire amount of ferric chloride into ferrous chloride ? Fe = 56, Cl = 35·5

3. (a) State the Law of Multiple Proportions for chemical combination. Give one example to illustrate it.

(b) Two oxides of a metal M were separately heated to constant weight in a current of hydrogen. Water formed was collected and weighed separately in two cases. The following results were obtained :—

(i) 0.795 gm. of first oxide yielded 0·18 gm. of water, (ii) 2·86 gm. of second oxide yielded 0·36 gm. of water. Show that these results are in agreement with the Law of Multiple Proportions.
4 + 6 = 10

4. (a) Define Standard solution and Normal solution.

(b) An aqueous solution is prepared by dissolving 40 gms. of NaOH in 1000 c.c. water. State with reasons whether this solution can be called a normal solution or not.

(c) 5·35 gm. of an impure sample of NH_4Cl is strongly heated with excess concentrated solution of caustic soda until all ammonia is given off. The resultant ammonia is completely absorbed in 120 c.c. N H_2SO_4 solution which further required 60 c.c. of 0·5N NaOH solution for complete neutralisation. Calculate percentage of pure NH_4Cl in the sample N = 14, Cl = 35·5.

5. (a) What information is obtained from the following equation : $Zn + H_2SO_4 = ZnSO_4 + H_2$

(b) Write down the limitations of chemical equation.

(c) A monobasic acid containing Nitrogen, Hydrogen and Oxygen only gave the following percentage composition by weight : N – 22·22%, H – 1·59%. Calculate the molecular formula of the acid. (N = 14)

6. (a) Find out the oxidation numbers of carbon in Methane and Carbon dioxide.

(b) Balance the following chemical equation by oxidation number method : $C + H_2SO_4 \rightarrow CO_2 + SO_2 + H_2O$

(c) Why is a chemical equilibrium called a dynamic equilibrium ?

(d) The chloride of a metal M contains 30% by weight of chlorine and is isomorphous with Potassium chloride (KCl). Calculate the atomic weight of M. (Atomic weight of Chlorine = 35·5)

Group – B

(Answer Q. No. 7 and any Three from the rest.)

7. (a) Name one drying agent and cite one example of its application.

(b) Name two bleaching agents and explain how they function.

(c) How is hardness of water expressed ?

(d) What is Aqua regia ? $1+2+1+1=5$

8. (a) Describe how Sulphur dioxide gas is prepared in the laboratory.

(b) Describe what happens when H_2S gas is passed separately through (i) a suspension of Iodine in water, and (ii) an acidified solution of Potassium dichromate solution.

Give equations in both cases. $6+2\times2=10$

9. In the Haber's process of manufacture of Ammonia the following reaction is used :—

$N_2+3H_2 \rightleftharpoons 2NH_3+24000$ Cal. (Heat)

(a) What pressure and temperature are maintained in the Haber's process for manufacture of Ammonia ? What catalyst and promoter are used ?

(b) Explain the justification of using the above mentioned pressure and temperature.

(c) State the sources of Nitrogen and Hydrogen.

(d) State what happens with balanced equations when ammonia gas is passed separately through (i) $CuSO_4$ solution, and (ii) $FeCl_3$ solution.

10. A soft white mental A (Atomic no. 11) when added to water produces a compound B soluble in water and a gas C. The gas C when passed over heated cupric oxide produces copper and water. The aqueous solution of B when added to an aqueous solution of Zinc sulphate produces a compound D which is precipitated. D becomes completely soluble when excess solution of B is added to it. (i) Identify A, B, C, and D (give the names only).

(ii) Describe the chemical reactions that occur in the above mentioned four stages and gives equations in all cases.

11. Explain why :—

(i) Silent electric discharge is passed in the preparation of Ozone from Oxygen. (ii) Most of the metals do not liberate hydrogen on reaction with Nitric acid. (iii) SO_3 gas is not absorbed in water but instead adsorbed in 98% H_2SO_4 acid during the manufacture of H_2SO_4 acid.

(iv) Phenolphthalein is not used as an indicator in the titration of an aqueous solution of Na_2CO_3 by an aqueous solution of HCl.

(v) In the laboratory method of preparation of PH_3 the air inside the flask (in which PH_3 is prepared) is replaced by coal gas.

$2 \times 5 = 10$

12. State with equations what happens when (any five)

(a) Iron powder is added to an aqueous solution of Ferric chloride solution containing hydrochloric acid. (b) Sulphur powder is heated with excess of concentrated solution of Caustic Soda. (c) Ozone gas is passed through Stanous chloride solution containing hydrochloric acid. (d) Conc. H_2SO_4 acid is allowed to fall drop by dorp over red hot pumice stone. (e) Hydrogen sulphide gag is passed through concentrated Sulphuric acid. (f) Manganese dioxide powder is heated strongly with concentrated Hydrochloric acid.

1985

Group—A

(Answer Question No. 1 and *any three* from the rest.)

1. (a) A compound containing two nitrogen atoms in its molecule has 30·43% of nitrogen. Calculate the molecular weight of the compound. (N = 14)

(b) How many atoms will be present in 0·05 mole of ozone ? 4+1=5

Or, (a) A gaseous hydrocarbon requires six times its own volume of oxygen gas for complete oxidation and produces four times its own volume of carbon dioxide gas. What is its formula ?

(b) Vapour density of a compound of empirical formula CH_2O is 90. What is the molecular formula of the compound ? 4+1=5
(C=12, H=1, O=16)

2. Ammonia contains 82·35% nitrogen, water contains 11·11% hydrogen and nitrogen peroxide contains 69·57% oxygen. Show that the above results can be explained with the help of a law of chemical combination. State this law. Explain the law with the help of Dalton's Atomic theory. 5+2+3=10

3. (a) State Le Chatelier's Principle.

Describe the effects of changes of pressure and temperature on the position of equilibrium of the following gaseous reaction :—
$H_2 + I_2 \rightleftharpoons 2HI - 13$ kcal.

(b) Volume of a given mass of a gas at fixed pressure changes from 1 litre to 1·3 litre due to a change of temperature from 0°C to 82°C. Determine the value of absolute zero (in centigrade scale) on the basis of above results. 6+4=10

4. (a) State Dulong and Petit's law. How is this law applied to find out the atomic weight of an element ? What are the limitations of the method ?

(b) 1·08 gm. of a metal produces 1·435 gm. of chloride. Specific heat of the metal is 0·059. What is its actual atomic weight ? (Cl=35·5)

5. (a) Calcium carbonate is precipitated when Sodium carbonate solution is added to Calcium chloride solution. Similar precipitation of Ferric carbonate does not occur when Sodium carbonate solution is added to Ferric chloride solution. Why is it so ? (b) What is an indicator ? Which indicators would you use for the following neutralisation reactions :—

(i) Hydrochloric acid by Sodium carbonate.

(ii) Oxalic acid by Sodium hydroxide.

(c) In what proportion by volume should a 0·5 N acid solution be mixed with a 0·3 N alkali solution to get a 0·05 N alkali solution ? 3+3+4=10

6. (a) What is oxidation number ? How will you differentiate it from valency ?

(b) Balance the following equation by oxidation number method :—$H_2S+SO_2 \rightarrow S+H_2O$.

(c) Zinc replaces silver from silver nitrate solution but silver cannot replace zinc from zinc nitrate Solution. Explain why.

5+3+2=10

Group—B

(Answer Question No. 7 and *any three* from the rest.)

7. (a) Give one reaction to show that Hydrogen can act as an oxidising agent. (b) Why cannot pure zinc be used for the preparation of hydrogen from dilute sulphuric acid ? (c) What is nascent hydrogen ?

Or, (a) Why is concentrated Sulphuric acid not used for the preparation of Hydrogen peroxide from Barium peroxide ? (b) Why is concentrated Hydrochloric acid not used for the preparation of nitric acid from potassium nitrate ? (c) What is laughing gas ?

2+2+1=5

8. (a) Describe the preparation of dry Sulphur dioxide gas in the laboratory.

(b) State (with chemical equations) the reaction of chlorine gas with the following reagents :—

(i) Hot and conc. Caustic soda Solution and

(ii) Aqueous solution of Sulphur dioxide 6+2+2=10

9. What is a chemical fertiliser ? Describe briefly the technical methods for the preparation of (a) a fertiliser containing nitrogen (b) a fertiliser containing calcium. 2+4×2=10

10. A sodium Salt (A) on heating gives a solid substance (B) and oxygen gas. B gives brown fumes (C) on being heated with dilute acid. When B is heated with Ammonium chloride, a colourless gas (D) and a solid residue (E) is obtained. A, on being heated with Ammonium chloride gives another colourless gas (F) and the solid residue (E). Identify A, B, C, D, E and F and write down the chemical reactions with equations. 3+7=10

11. State with chemical equations, what happens when (*any five*)

(a) Water is added drop by drop into a mixture of red phosphorus and iodine. (b) Hydrogen sulphide gas is passed into a solution containing cupric chloride and zinc chloride acidified with dilute hydrochloric acid. (c) Hydrogen peroxide is added to a solution of potassium dichromate acidifed with dilute sulphuric acid. (d) Sulphur is boiled with concentrated nitric acid. (e) Powdered charocoal is heated with concentrated nitric acid. (f) Ammonia solution is added gradually to a solution of silver nitrate. (g) sodium nitrite solution is heated with aluminium powder and caustic soda.

$2 \times 5 = 10$

12. Explain why (*any five*) :—

(a) Coal gas may be poisonous. (b) While diluting sulphuric acid is added slowly to water. (c) Sulphur dioxide has no bleaching action in absence of moisture. (d) Nitrogen obtained from air is slightly heavier than nitrogen obtained from ammonium nitrite. (e) Carbon dioxide is a gas, while silicon dioxide is a solid. (f) Diamond is very hard while graphite is soft. (g) Hydrogen iodide cannot be dried by concentrated sulphuric acid. $2 \times 5 = 10$

1986

Group—A (Answer *any four* questions)

1. The percentages of oxygen in two oxides of a metal are 22·22 and 30 respectively. Show that the above result follows a law of chemical combination. State the concerned law. If the formula of the second oxide be M_2O_3 find that of the first.

$6+2+2=10$

2. (a) State Avogadro's hypothesis and establish the relationship between molecular weight and vapour density of a gas with its help.

(b) 1·2 gm of a gas occupies 1000 mililitre at 27°C and 700 mm. pressure of mercury. The gas is an element and its molecules are diatomic. What is the weight of one atom of this gas ?

$2+4+4=10$

3. (a) What do you understand by the equivalent weight of an element ? Prove that the atomic weight of an element is equal to or simple multiple of its equivalent weight.

(b) 20·55 ml. of dry hydrogen gas at a standard temperature and pressure are produced by the action of 0·06 gm of a metal with dilute sulphuric acid. The solution obtained as a result of this reaction gives on evaporation and subsequent cooling a crystalline substance which is isomorphous with $FeSO_4, 7H_2O$. Determine the equivalent weight and exact atomic weight of the metal.

$5+5=10$

(d) Air is a mechanical mixture but not a chemical compound. Silicon dioxide is an acidic oxide.

(e) Phosphine has basic properties. $2 \times 5 = 10$

12. (a) How Sulphuric acid is manufactured by contact process ?

(b) Describe with equations how Urea is manufactured from Ammonia.

(c) State what happens when Orhophosphoric acid is heatel slowly to a high temperature. Give equations. $5+3+2=0$p

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4. (a) State Dalton's Law of partial pressure.

(b) A compound contains 10·04% carbon, 0·84% Hydrogen and 89·12% Chlorine. Determine the empirical formula of the compound.

(c) 1 gm of pure $CaCO_3$ is dissolved completely in 40 ml. of a hydrochloric acid solution. The resultant solution requires 40 ml of 0·5 N. NaOH solution for complete neutralisation. Find out the strength of Hydrochloric acid solution.

(d) Which indicator would you use during the neutralisation of Acetic by sodium hydroxide? $2+3+4+1=10$

5. (a) Find the value of molar gas constant R in litre atmosphere after stating the units P, V and T.

(b) Explain with reasons why an aqueous solution of NH_4Cl reacts acidic.

(c) Show reasons why magnesium can liberate Hydrogen from an aqueous solution of Hydrochloric acid while copper cannot liberate Hydrogen.

(d) 10 ml. of a gaseous Hydrocarbon were exploded with 25 ml. of Oxygen and cooled. The gas mixture occupied a volume of 15 ml. On treatment with KOH there was a further contraction of 10 ml. Find the molecular formula of the Hydrocarbon.

$2+2+2+4=10$

6. (a) Express the equilibrium constant of the reaction :

$$N_2(g)+3H_2(g)\rightleftharpoons 2NH_3(g)$$

in the forms Kp and Kc and find out rhe relation between these two constants.

(b) Determine the oxidation number of Mn in K_2MnO_4.

(c) Balance by oxidation number method :

$$FeCl_3+H_2S=FeCl_2+S+HCl.$$

(d) "Concentration of Sodium Chloride Solution is expressed in formality but not in molarity."—Give reasons. $3+2+3+2=10$

Group—B (Answer *any four* questions)

7. Mixture of a white solid A and a black solid B gives on heating a white solid C and a gas D while B remains unchanged. If A alone is heated C and D are obtained but it required higher temperature and the reaction proceeds slowly. When aqueous solution of Silver Nitrate is added to an aqueous solution of C, a white precipitate of E is obtained. E is completely soluble in excess of ammonia solution. The gas D when mixed with Nitric Oxide gas forms another red coloured gas F.

(i) Identify A, B, C, D, E and F. Write down the names only.

(ii) For each chemical reaction give equations only.

(iii) What is the function of B while producing C and D from A ?

(iv) Name another substance which will perform the same function as B. 3+5+1+1=10

8. (a) Describe the method of preparation of Chlorine gas in the laboratory.

(b) With the help of a chemical reaction show that Iodine acts as an oxidising agent.

(c) How can a small quantity of chlorine mixed with oxygen gas be removed ? 6+2+2=10

9. Explain the following statements with reasons :—

(a) Carbon dioxide gas cannot extinguish fire caused by burning magnesium metal.

(b) If one touches white phosphorus, one's hands are to be washed with copper sulphate solution.

(c) Sulphur dioxide have both oxidising and reducing properties.

(d) Hydrogen bromide cannot be prepared by the action of concentrated sulphuric acid on sodium bromide.

(e) Ozone gas is prepared by silent electric discharge through oxygen. 2×5=10

10. State what happens when with equations (*any five*) :—

(a) Potassium Nitrite solution is added to Potassium iodide solution acidified with dilute sulphuric acid.

(b) Phosphine gas is passed into acidified copper sulphate solution.

(c) Sodium Formate is heated with concentrated sulphuric acid.

(d) Concentrated Sulphuric acid is added to a mixture of solutions of Ferrous Sulphate and Potassium Nitrate.

(e) Aqueous solution of hydrogen peroxide is added to alkaline Potassium ferricyanide solution.

(f) Ozone gas is passed through stannous chloride solution containing hydrochloric acid. 2×5=10

11. How will you show that (*any five*) :—

(a) Nascent Hydrogen is more powerful reducing agent than ordinary Hydrogen.

(b) Sulphur dioxide contains sulphur.

(c) Nitric acid contains hydrogen.